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.

CAMBRIDGE, MASS. RECEIVED APRIL 1, 1946

[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

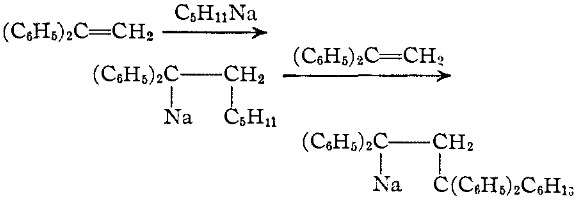
The reaction of organosodium reagents with styrene and *as*-diphenylethylene has been studied to see if any parallelism exists with the action on dienes, especially with respect to any 1,2-process. The results reported in this paper show (a) that organosodium reagents, such as amylsodium and phenylsodium, 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).

adducts. Some metalation of the mono product occurs presumably in a benzene ring. Carbonation then gives a dicarboxylic acid.

The general structure of the mono addition products of organoalkali metal compounds with diphenylethylene has been proven by earlier workers.[2] We have assumed similar structures for our products and have employed a method of separation of the acids based on such an assumption. The two tertiary acids derived as a result of the addition reactions are weaker than the dicarboxylic acid derived from addition and metalation. Judicious use of carbon dioxide and ether with the solution of sodium salts displaces all acids which have tertiary carboxyl groups only; compounds that have primary carboxyl groups are segregated in the aqueous layer. This method, with suitable supplements, paves the way toward determination of the three acid products.

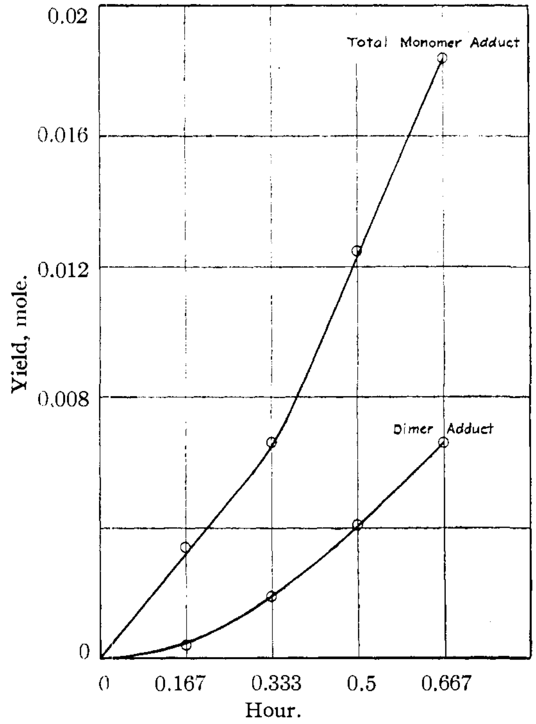

Fig. 1.—Yield *vs.* time curves for the reaction of *unsym.*-diphenylethylene with amylsodium.

The lithium-, sodium- and potassium-amyl compounds do not add to diphenylethylene at the same rate, nor do they give the same proportions of mono and di adducts (see Table I). Under comparable conditions the relative reactivities are as 0.003 to 1 to 3, respectively, for the total amounts of adducts. Amyllithium gives no dimer and no metalated monoadduct. These results are consistent with the lower reactivity expected of lithium compounds. Conversely, amylpotassium is more reactive than amylsodium. The last comparison was made at 0° in order to avoid complications from a possible decomposition, since amylsodium has already been shown[5] to decompose slowly at room temperature and amylpotassium should be even less stable.

TABLE I

YIELDS FROM REACTIONS OF AMYLALKALI-METAL COMPOUNDS WITH *as*-DIPHENYLETHYLENE

Metal $C_5H_{11}M$ compound	Temp., °C.	Moles of $C_5H_{11}M$ used	Total moles of addition products
$C_5H_{11}Na$	25	0.0474	0.0344
$C_5H_{11}Li$	25	.0526	.0001
$C_5H_{11}Na$	0	.0477	.0031
$C_5H_{11}K$	0	.0234	.0091

Phenylsodium will not add to 1,1-diphenylethylene under conditions which give good yields with amylsodium. Given time, a very small amount of addition occurs. No metalation of the adduct takes place. The general failure of phenylsodium to add is peculiar in that benzylsodium, which is less reactive in substitution reactions, adds readily. These results parallel those found[6] with butadiene; amylsodium adds readily to the diene, phenylsodium does not; the more stable benzylsodium does. Apparently the addition reactions of phenylsodium are inhibited for some special reason.

The Induction Period.—A short induction period is evident in the graph of yield *vs.* time in the addition of amylsodium to *as*-diphenylethylene (see Fig. 1). The growth reactions of mono and di compounds are simultaneous, and the equations are

$$R + O \longrightarrow M$$
$$O + M \longrightarrow D$$

where R is the organometallic reagent, O is the olefin, M is the mono-adduct and D is the di-adduct. Since metalation of the mono-adduct is a secondary reaction, the moles of metalated product can be added to the quantity of mono adduct in order to get the total amount of the latter. The di adduct is derived from the mono also. Data are shown in Table II.

TABLE II

ADDITION PRODUCTS OF AMYLSODIUM WITH *as*-DIPHENYLETHYLENE WITH THREE DIFFERENT AMOUNTS OF AMYLSODIUM

	Moles per liter 1	2	3
Amylsodium[a]	0.155	0.240	0.157
1,1-Diphenylethylene	.227	.227	.341
Mono adduct isolated	.0209	.0246	.0258
Metalated mono adduct	.0045	.0064	.0064
Di adduct isolated	.0124	.0121	.0279
Total mono adduct formed	.0378	.0431	.0601
Ratio mono to di	1.7	2.0	.92

[a] The amount of amylsodium is calculated as the sum of all the carboxyl groups in the reaction products.

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(5) Morton and Newey, THIS JOURNAL, **64**, 2247 (1942).

(6) Morton, Patterson, Donovan and Little, *ibid.*, **67**, 2224 (1945).

The total adduct in this table represents, of course, the total amount of mono adduct which has been formed during the reaction.

An increase of 55% in the concentration of amylsodium produces only a small increase (15%) in the total adduct, but a change of 50% in the concentration of the olefin increases the total adduct by as much as 58%. The over-all rate of formation of mono adduct, therefore, is approximately proportional to the amount of olefin, *O*. This first order effect contrasts with the second order expression used by Ziegler[4] for the reaction between alkyllithium compounds and this same olefin, but Ziegler's alkali metal reagent was soluble, whereas ours is insoluble in the medium used. The formation of the dimer adduct can be regarded as a second order effect between the mono adduct and the olefin. The over-all equations are

$$\mathrm{d}M/\mathrm{d}t = k_1O - k_2MO \qquad (3)$$

$$\mathrm{d}D/\mathrm{d}t = k_2MO \qquad (4)$$

The integration of (3) with *O* constant (a reasonable assumption at the beginning of the reaction) shows that *M* increases when *O* increases.

$$M = k_1/k_2(1 - e^{-k_2tO}) \qquad (5)$$

The rate of change of *M* with respect to *D* as given by (3) over (4) in equation (6) below

$$\frac{\mathrm{d}M}{\mathrm{d}D} = \frac{k_1 - k_2M}{k_2M} \qquad (6)$$

shows, however, that an increase in *M* decreases the rate of change of *M* with respect to *D*. Hence as the amount of olefin, *O*, is increased, the amounts of mono and di adducts increase differently and the ratio *M*/*D* decreases. Of a number of possibilities tried these equations best represent the true state of affairs during the addition of amylsodium to the ethylene compound, although they do not hold precisely because of the slight influence of *R* on the reaction and because of the presence of the metalation reaction.

The values of k_1 were calculated from the equation

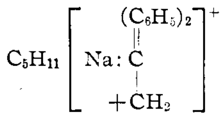
$$\frac{\Delta(M + D)}{\Delta t} = k_1O \qquad (7)$$

in which time is in hours and *M*, *D* and *O* are in moles per liter. This equation is derived from the sum of the two rate equations given above and by conversion of the differentials to finite quantities. The value of k_2 is determined from the equation

$$\Delta D/\Delta t = k_2MO \qquad (8)$$

Any deviations in k_2 can be attributed to some of the approximations necessary in the use of the equations.

The graph (Fig. 1) shows that a small but definite induction period is present in the formation of the mono adduct. This period may conveniently be attributed to the formation of an intermediate complex shown below in which a pair of electrons of the unsymmetrical diphenylethylene are drawn toward the sodium.



$$\mathrm{C_5H_{11}}\left[\begin{array}{c}(\mathrm{C_6H_5})_2\\ \|\\ \mathrm{Na:C}\\ |\\ +\mathrm{CH_2}\end{array}\right]^+$$

This complex is analogous to those probably formed with tertiary amines, as described in the next section, and accords with the strong tendency of the sodium ion to attract electrons. The attraction of sodium for the amyl anion would thus be loosened; the electrostatic bond would be weaker; addition would occur more readily.

Effect of Triethylamine.—Triethylamine accelerates the addition of amylsodium to 1,1-diphenylethylene. For instance, 0.05 mole of the amine added to an approximately equal proportion of amylsodium increases the yield of total adduct from 0.0066 mole to 0.0293. No induction period is present.

As the ratio of triethylamine to amylsodium is increased from 1 to 2 to 3, the molal ratio of mono to di adduct decreases from 3.7 to 2.6 to 2.3. The faster rate of formation of the mono compound is reflected by an accelerated rate for the dimer adduct and the formation of the latter in turn is accelerated by the presence of the amine. Figure 2 shows this increase in both types of products. The flattening of the curve for the monomer at three equivalents of the amine is caused by the fact that the reaction is largely completed.

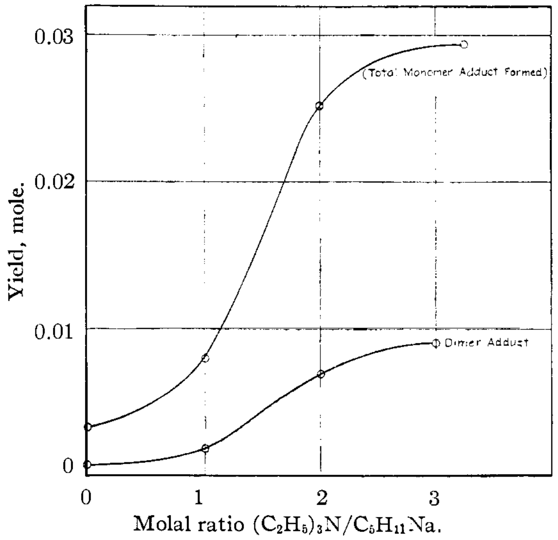


Fig. 2.—Yield of adducts *vs.* molar ratio $(C_2H_5)_3N/C_5H_{11}Na$.

The explanation for the accelerated rate probably lies in the formation of the complex

$$\mathrm{C_5H_{11}[Na:N(C_2H_5)_3]^+}$$

which functions in the same manner as suggested for the complex between the sodium ion and 1,1-diphenylethylene.

The object of this paper was to shed light on the possible action of organosodium compounds with butadiene by a study of the reaction of such reagents on styrene and diphenylethylene. These two hydrocarbons can be regarded as phenylethylene and diphenylethylene, respectively, and butadiene may be regarded as vinylethylene. The results of the study show several points of similarity, as far as addition reactions are concerned, between diphenylethylene and butadiene, in that phenylsodium adds to neither, amylsodium and benzylsodium add to both, triethylamine accelerates the addition reaction, and intermediate products are readily isolable. The addition process with diphenylethylene is limited to two steps but this fact is not surprising in view of the stability imparted by two phenyl groups in that olefin. On the other hand, very little similarity exists between styrene and butadiene, except in one respect, namely, that phenylsodium causes a catalytic polymerization in both cases. The action on styrene, however, appears to induce a normal polymerization, while the action on butadiene gives a poor quality of rubber (see next paper, V). The similarity between 1,1-diphenylethylene and butadiene suggests, but does not prove, of course, that addition to the diene is 1,2-, and this opinion accords with the other evidence of high percentage of 1,2-addition or its equivalent as reported in the third paper of this series.

Apart from the bearing which these results have on the process of 1,2-addition, several new compounds were prepared and characterized. Methyl α,α-diphenylcaprylate was prepared because the corresponding acid proved difficult to crystallize. Three polymorphic forms of $\alpha,\alpha,\gamma,\gamma$-tetraphenylcapric acid, the carbonation product of the adduct of one amylsodium with two equivalents of 1,1-diphenylethylene, were isolated. The two lower melting forms were readily converted to the highest one by heat. The corresponding ester of this acid was also obtained. The dimeric adduct of butylsodium and 1,1-diphenylethylene yielded two polymorphic forms of $\alpha,\alpha,\gamma,\gamma$-tetraphenylpelargonic acid. Benzylsodium and 1,1-diphenylethylene yielded, subsequent to carbonation, $\alpha,\alpha,\gamma,\gamma,\omega$-pentaphenylcaproic acid. In general the dimeric adducts were crystallized more easily than were the monomeric adducts, although the occurrence of polymorphism was troublesome until recognized.

The authors are grateful to Professor W. H. Stockmayer for material assistance in the interpretation of the kinetic data. They are also indebted to the Research Corporation for financial support of the larger part of this study and to The Rubber Reserve Company for support of a smaller part.

Experiments

Organoalkali Metal Reagents.—All preparations were carried out with the high-speed stirring apparatus in a 500-ml., two-creased inverted cone bottom flask similar to that employed in this Laboratory.[7] One alkyl or aryl chloride to two atoms of sodium was used in all cases. Amylsodium and butylsodium were thus prepared according to the general method described earlier.[1] Phenylsodium was similarly made from chlorobenzene. Benzylsodium was made by the reaction of amylsodium with toluene.[8]

In the preparation of the lithium compounds butane was used as the inert atmosphere instead of nitrogen because the nitrogen reacts with lithium metal. The preparation of amylpotassium is the same as that described elsewhere[9] in this series.

Variations from the general processes will be described as necessary.

Styrene.—The Eastman Kodak Co. grade was freshly distilled before use. One equivalent of styrene, dissolved in *n*-pentane, was added dropwise to a pentane suspension of amylsodium or phenylsodium in the high speed stirring apparatus. The time in different experiments was varied from one hour to five hours. At the end of that period the contents were forced on solid carbon dioxide and after a time water was added. The aqueous layer contained no carboxylic acids other than those derived by carbonation of the reagent. The water insoluble portion contained the styrene polymer. Combustion data, used to determine the number of carboxyl groups, showed one per 1.03 styrene units for the polymer produced by amylsodium and one per 5.7 styrene units for the corresponding one from phenylsodium. The polymer from amylsodium was soluble in 5% methyl alcoholic potassium hydroxide; that from phenylsodium was only partially soluble.

Amylsodium and 1,1-Diphenylethylene.—The operations herein described are the same as those used in the kinetic studies described later in this section. They are presented in some detail because of the care which must be exercised for quantitative measurements.

The desired quantity of 1,1-diphenylethylene,[10] usually one and a half equivalents, was dissolved in *n*-pentane suspension of amylsodium in the high-speed stirring apparatus. The stirring was maintained at 10,000 to 11,000 r. p. m. The color changed progressively from the blue of amylsodium to brown, to orange, to brick-red.

At the conclusion of the reaction the contents were forced by nitrogen pressure into a flask which contained solid carbon dioxide and the resulting mixture was stirred gently until the temperature rose to that of the room. The remaining carbon dioxide was swept from the flask by nitrogen, 200 ml. of water was added—the first small portion with caution—and 20 ml. of 1 *N* potassium hydroxide was finally added. The two layers were separated and the aqueous portion freed from the neutral organic material by extraction with four successive 100-ml. portions of petroleum ether. Any further quantity of neutral product or solvent was then removed by steam distillation.

The mixture of acids thus obtained was separated into strong and weak fractions (primary and tertiary acids) by bubbling carbon dioxide slowly for one hour into the aqueous layer in the presence of 200 ml. of ethyl ether which served to extract the weakest acids as fast as they were liberated. The layers were separated, 100 ml. of ether was added to the aqueous portion, and carbon dioxide was once more passed in for fifteen minutes. This last series of operations was repeated once more after which the three solutions were shaken with 50 ml. of 0.5 *N* sulfuric acid in order to eliminate all sodium salts that might have been carried into the upper layer. Small quantities of caproic acid were apt to be forced into the ether layer by the carbon dioxide treatment. They were removed by shaking with sodium bicarbonate solution and then with water. The alkaline extract was added to the remainder of the alkali solution.

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[7] Morton, Davidson and Newey, THIS JOURNAL, **64**, 2240 (1942).

[8] Morton, Little and Strong, *ibid.*, **65**, 1339 (1943).

[9] Morton and Letsinger, *ibid.*, **67**, 1537 (1945).

[10] Gilman and Blatt, "Organic Syntheses," Coll. Vol. I, p. 226.

The ether solution was dried over anhydrous magnesium sulfate, filtered and evaporated on the steam-bath. Traces of volatile material were eliminated at 150° (2 mm.). As much as 0.1 g. of caproic acid was sometimes recovered at this point when the consumption of amylsodium was less than 60%. The residue was a mixture of the two tertiary carboxylic acids, one from the mono adduct and the other from the di adduct. The neutralization equivalent could be used frequently to calculate the proportions of these two products. The usual procedure, however, was to separate them by fractional crystallization. As an example a 250–300 mg. sample in 70 ml. of boiling methanol was diluted dropwise with 17 ml. of water. The solution was allowed to cool slowly, and four days later the mixture was filtered. The product from the dimeric adduct was recovered quantitatively save for its solubility in the medium.

The mother liquor from this treatment contained the α,α-diphenylcaprylic acid which proved difficult to crystallize. The corresponding product from a larger scale, but otherwise identical, preparation was converted to the methyl ester by diazomethane. The ester distilled at 159.5 to 160 at 2 mm. and had a refractive index of $n^{25}\text{D}$ 1.5420.

Anal. Calcd. for $C_{21}H_{26}O_2$: C, 81.3; H, 8.39. Found: C, 81.4, 81.3; H, 8.48, 8.51.

The precipitate from the above treatment was recrystallized from dilute methanol. The product proved to be polymorphous. Mixtures which consisted predominantly of one or another form were obtained by chance; no change of solvent or temperature of crystallization proved useful as a sure means for obtaining a specific form. The highest melting form could, however, be obtained from either of the two lower forms by heating to 215° and cooling with stirring. Solidification occurred at 193°. The forms and changes were observed chiefly with the aid of a Kofler micro hot stage apparatus. The lowest melting isomorph was obtained as rhomboid shaped crystals that melted at 184–185° cor.

Anal. Calcd. for $C_{34}H_{36}O_2$: C, 85.7; H, 7.56. Found: C, 85.6, 85.8; H, 7.44, 7.63.

The second form crystallized as feathers which melted at 192.5 to 194.5° cor.

Anal. Found: C, 86.1, 86.0; H, 7.80, 7.86.

The highest melting compound was obtained in the shape of hexagons which melted at 212–213° cor.

Anal. Found: C, 85.8, 85.6; H, 7.94, 7.66.

The methyl ester, methyl α,α,γ,γ-tetraphenylcaprate, was obtained from diazomethane and the acid. It was readily crystallized from methanol and melted at 120–121.5° cor.

Anal. Calcd. for $C_{35}H_{38}O_2$: C, 85.7; H, 7.65. Found: C, 85.9, 85.6; H, 7.94, 8.25.

The alkaline layer which contained the primary acids was found, after appropriate separation, to consist of a mixture of caproic acid and a higher molecular weight acid, the neutralization equivalent of which usually varied from 187 to 189. The calculated value for $C_6H_5(C_6H_4CO_2H)(C_5H_{11})CCO_2H$ is 170. The quantity was usually very small and was regarded as derived from a metalation product of the mono adduct.

Amyllithium and 1,1-Diphenylethylene.—Amyllithium, derived from 0.062 mole (6.6 g.) of amyl chloride and 0.127 g. atoms (3.3 g.) of lithium was allowed to react in the usual manner with 0.075 mole (13.5 g.) of 1,1-diphenylethylene. The addition time was one hour, the temperature was 25°. The combined yield of tertiary acids was 0.29 g. The recovered caproic acid was 3.8 g. (0.0328 mole). By calculation from all the carboxyl groups found in the final products, the quantity of amyllithium was 0.0329 mole which amounted to 53% yield from amyl chloride. The percentage which added to the olefin was, therefore, only 0.3.

Amylpotassium and 1,1-Diphenylethylene.—Amylpotaissum derived from 0.091 mole (9.7 g.) of amyl chloride and 0.186 g. atom (7.3 g.) of metal was allowed to react with 0.075 mole (13.5 g.) of 1,1-diphenylethylene. The addition time was one hour; the temperature was 0°. The combined tertiary carboxylic acid fraction contained 2.7 g. and the neutralization equivalent was 355. This value corresponded to 0.0051 mole of the mono adduct and 0.0025 mole of the di-adduct. The recovered caproic acid was 2.5 g. or 0.0218 mole. The yield of amylpotassium from amyl chloride was 36% and the quantity which added to the olefin was 28% of the total organopotassium compound available.

Phenylsodium and 1,1-Diphenylethylene.—Phenylsodium was made in 80% yield from 0.132 mole (14.8 g.) of chlorobenzene and 0.270 g. atom (6.2 g.) of metal. The reaction of this reagent with 0.0922 mole (16.6 g.) of diphenylethylene took place during one hour of addition time and eighteen more hours of stirring. The temperature was 25 to 26.5°. In spite of this extremely long period only 5% of phenylsodium added to the olefin to give 1.5 g. of a mixture of the tertiary acids. The neutralization equivalent proved this material to be derived from the mono adduct. When the reaction was allowed to proceed for the usual time (one hour or less) no addition product was obtained.

Butylsodium and 1,1-Diphenylethylene.—Butylsodium (0.0505 mole) was prepared from 0.0809 mole (7.5 g.) of *n*-butyl chloride and 0.166 g. atom (3.7 g.) of sodium. The reaction with 0.075 mole (13.5 g.) of 1,1-diphenylethylene for one hour at 25° yielded 6.2 g. of the mixture of tertiary acids which had a neutralization equivalent of 377, 3.1 g. of valeric acid and 0.69 of the acid derived from the metalated mono adduct. A 2.2-g. sample of the mixture of tertiary acids was recrystallized from a mixture of 220 ml. of methanol and 52 ml. of water.

The crystals thus obtained were dimorphous. The small low melting form melted at 180.5 to 185° cor. and changed to the high melting variety at 212°.

Anal. Calcd. for $C_{33}H_{34}O_2$: C, 85.7; H, 7.36. Found: C, 85.9, 85.9; H, 7.45, 7.51.

The high melting form of α,α,γ,γ-tetraphenylpelargonic acid formed large crystals which melted at 206–209° cor.

Anal. Calcd.: neut. equiv., 462. Found: C, 85.9, 85.7; H, 7.36, 7.36; neut. equiv., 461.

The carboxylic acid, the neutralization equivalent of which corresponded to the mono-adduct, was obtained only as an amorphous product.

Benzylsodium and 1,1-Diphenylethylene.—Amylsodium was prepared from 0.14 mole (3.5 g.) of amyl chloride and two equivalents of sodium. Toluene (45.3 g.) was added to the suspension at −10°, the mixture was warmed to 30° and maintained there for three hours with stirring in order to form benzylsodium. The resulting suspension of benzylsodium was cooled to 25°, a solution of 13.5 g. (0.075 mole) of 1,1-diphenylethylene in pentane was added over a one hour period, and stirring was continued for an additional hour. The mixture of tertiary acids weighed 7.5 g. The neutralization equivalent was 393 corresponding to 0.0109 mole of the acid from the mono-adduct and 0.0082 mole from the di-adduct. The mono acid, recrystallized from ligroin, melted at 183 to 184.5° cor. and was identical as far as could be judged with the α,α,γ-triphenylbutyric acid prepared by Schlenk and Bergmann.[11] The di acid was obtained as a crystalline material which melted at 227–232° cor. after successive crystallizations from aqueous methanol, aqueous acetic acid (twice) and ligroin. The product corresponds to α,α,γ,γ,ω-pentaphenylcaproic acid.

Anal. Calcd. for $C_{36}H_{32}O_2$: C, 87.1; H, 6.45. Found: C, 87.0, 87.0; H, 6.99, 6.80.

Kinetic Measurements.—The method of carrying out the reactions and separation of products was the same as described in the section on the reaction of amylsodium with 1,1-diphenylethylene. The diphenylethylene was added at one time rather than dropwise in order to have a suitable starting time for the reaction. Great care was taken to account quantitatively for all products present. Where the products were isolated by crystallization, as was

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[11] Schlenk and Bergmann, *Ann.*, **479**, 87 (1930).

TABLE III

VELOCITY CONSTANTS FOR THE REACTION OF AMYLSODIUM WITH *as*-DIPHENYLETHYLENE AT 25°

	Without triethylamine				With one equivalent of triethylamine		
Time, hr.	0.167	0.333	0.5	0.667	0.0833	0.167	0.333
R[a]	0.157	0.150	0.155	0.156	0.144	0.153	0.157
O	.227	.227	.227	.227	.227	.227	.227
M	.0064	.0106	.209	.0300	.0164	.0279	.0640
D	.0012	.0048	.0124	.0200	.0052	.0145	.0242
M_s	.0027	.0045	.0045	.0055	.0027	.0045	.0064
k_1	.28	.28	.57	.65	1.4	1.2	1.5
k_2	10	12	15	11	36	28	10

[a] R = reagent = amylsodium; O = olefin = 1,1-diphenylethylene; M = monomeric adduct; D = dimeric adduct; M_s = substituted jonomeric adduct.

usually the case, proper allowance was made for the solubility of the solids in the solvent used. Some pertinent data are recorded in Table III. The graph in Fig. 1 shows the induction period.

Effect of Triethylamine.—Triethylamine (Eastman Kodak Co.) was distilled before use. The general procedure was the same as described above save for the addition of the amine. The effect of one equivalent of triethylamine on the respective velocities is shown in Table III. The effect of two and three equivalents is shown in Fig. 2. The period of the reaction was ten minutes. Triethylamine accelerates somewhat the addition of phenylsodium to diphenylethylene.

Summary

Amylsodium and phenylsodium cause styrene to polymerize. No addition products were isolated under conditions extremely favorable for such a result.

Amylsodium adds readily to 1,1-diphenylethylene. A mono- and di-adduct are formed. Some metalation of the mono product results.

Amyllithium is less reactive and amylpotassium is more reactive than amylsodium in the addition reaction.

Butylsodium and benzylsodium also add to the ethylene compound but phenylsodium scarcely reacts.

An induction period is present in the reaction between diphenylethylene and amylsodium.

The formation of the mono adduct is approximately independent of the quantity of the insoluble organoalkali metal reagent but is directly dependent on the concentration of the ethylene. The formation of the di-adduct is dependent on the concentration of the mono adduct and the ethylene.

Triethylamine accelerates the addition reaction.

CAMBRIDGE, MASS.

RECEIVED APRIL 1, 1946

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

Polymerization. V. The Catalytic Polymerization of Butadiene by Phenylsodium and Amylpotassium

BY AVERY A. MORTON AND ROBERT L. LETSINGER

Previous work[1] in this Laboratory has shown that the polymerization of butadiene with amyl- and benzylsodium can be so carried out that intermediate products of low molecular weight are obtained; but that, curiously enough, the reaction with phenylsodium gives rubber with little, if any, such intermediates even though the conditions are exceptionally well suited for their isolation. The present examination of this reaction indicates (a) that phenylsodium and amylpotassium, the latter under special conditions, exert an action that is catalytic and unrelated to the stepwise addition process by which amylsodium operates, (b) that complex formation between phenylsodium and sodium chloride and between amylpotassium and potassium chloride may play a part in the catalytic process and (c) the effect that benzene or triethylamine exerts on the polymerization induced by amylsodium is not the same as is exerted on the polymerization induced by phenylsodium. Mercury has a deleterious effect on the catalytic activity of phenylsodium.

Phenylsodium.—If phenylsodium polymerizes butadiene by the stepwise addition mechanism shown by amylsodium, the rates of the initiation reaction, k_i, caused by these two sodium containing reagents will differ widely, but the rates of chain growth, k_n, will either be in the same relative order if the respective influences of the amyl and phenyl groups are continued or will be equal if these influences are nullified over the lengthened chain. Now the k_i value for amylsodium must be reasonably high because a sizable quantity of the first adduct and of higher adducts can be isolated without difficulty[1,2] when butadiene is added dropwise to a large excess of the reagent and the mixture is then carbonated. Moreover, the addition reaction of this reagent with diphenylethylene, a compound unusually well suited for a

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

[2] Morton, Brown and Magat, THIS JOURNAL, **68**, 161 (1946).