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This invention relates broadly to a novel process for the preparation of dimerized products from dienes and to the compositions obtained thereby, and, more specifically, relates to a process wherein conjugated aliphatic diolefins are selectively reacted to give high yields of dimerized derivatives relatively free from more highly polymerized products.

This application is a continuation-in-part of application Serial No. 382,456, filed September 25, 1953 (now U.S. Pat. No. 2,816,916), which is a continuation-in-part of Serial No. 333,354, filed January 26, 1953 (now abandoned).

It is an object of this invention to react aliphatic conjugated diolefins selectively with an alkali metal such as sodium or potassium in finely dispersed form to obtain the dimetallo derivatives of dimerized dienes having twice the number of carbon atoms of the starting diolefins.

Another object of this invention is to carry out a subsequent step by carbonating the dimetallo derivatives so obtained to form the salts of dicarboxylic acids derived from the dimerized dienes and having two additional carbon atoms. The resulting salt products may be converted to acids and the latter isolated, or the salt products may be separated as such and then converted to acids.

A further, more specific object is to selectively dimerize butadiene using finely dispersed sodium and in the presence of an ether reaction medium and a small amount of a polycyclic-aromatic hydrocarbon to obtain disodio-octadienes and, if desired, thereafter to carbonate said product to obtain aliphatic C_{10} dicarboxylic acids and salts thereof.

It has been heretofore proposed to prepare mixtures of organic acids by reacting an aliphatic diolefin such as butadiene with sodium or potassium and carbon dioxide in a special solvent and to hydrolyze the compounds so obtained. In this prior work, the sodium was used in massive form, with provision for an abrading or scraping of the sodium surfaces with a rotating brush or scraper. Experimental studies of the products so obtained show that they are complex mixtures of polymeric acids having a range of relatively high molecular weights. Large quantities of polymers of the Buna rubber type are also produced. These materials have relatively little industrial value, and are entirely different from the selectively dimerized products obtained by this invention.
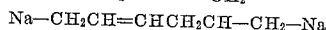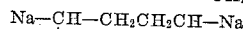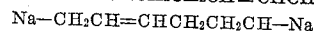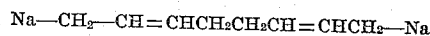
The present invention is carried out by initially treating an aliphatic conjugated diolefin with finely dispersed sodium or potassium in the liquid ether medium and in the presence of a relatively small amount of a polycyclic aromatic hydrocarbon at a temperature below 0° C.

The disodio dimer product thus obtained is then carbonated at a temperature below 0° C., to give the salts of the desired dicarboxylic acids in high yields and selectivity.

The net result of the initial step is a reaction which yields a dimerized product. In the case of sodium and butadiene, this product comprises the disodium derivatives of the aliphatic octadienes. From a study of structures of the saturated diacids arising therefrom, it

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has been shown that this selective dimerization may yield the following products:

$$Na—CH_2—CH=CHCH_2CH_2CH=CHCH_2—Na$$

$$Na—CH_2CH=CHCH_2CH_2CH—Na$$
$$\overset{|}{CH}$$
$$\overset{||}{CH_2}$$

$$Na—CH—CH_2CH_2CH—Na$$
$$\overset{|}{CH} \qquad \overset{|}{CH}$$
$$\overset{||}{CH_2} \qquad \overset{||}{CH_2}$$

$$Na—CH_2CH=CHCH_2CH—CH_2—Na$$
$$\overset{|}{CH}$$
$$\overset{||}{CH_2}$$

Using the herein described selective process, it is possible to obtain combined yields of the above C_{10} dimerized products ranging up to 80–90% based on the butadiene.

Subsequent carbonation of the above disodium derivatives, followed by hydrogenation and acidification, yields, respectively, sebacic acid, 2-ethylsuberic acid, 2, 2'-diethyladipic acid, and 3-ethylsuberic acid.

The diolefins which are useful for this improved process include any aliphatic conjugated diolefin such as, for example, butadiene, isoprene, dimethyl butadiene, the pentadienes, as the methyl-1,3-pentadienes, and the like. In general, it is desirable to use the conjugated diolefins having from 4 to 8, inclusive, carbon atoms. The method is particularly well adapted to the use of butadiene as the diolefin.

Either sodium or potassium may be used as the alkali metal reactant. The use of sodium is preferred over potassium since sodium gives excellent selectivity and yields of dimerized products, and it is cheaper and more readily available. Chemically pure sodium is not essential, however, since mixtures containing a major proportion of sodium are also useful. Thus, alloys of sodium and potassium, sodium and calcium, and sodium and lithium can be used.

One factor essential to the successful production of the dimerized derivatives is the use of the alkali metal in finely dispersed form. A sodium dispersion in which the average particle size is less than 50 microns is necessary for satisfactory dimerization since bulk sodium instead of dispersed sodium either yields no product or results largely in the formation of highly condensed diene polymers. The formation of these unwanted polymeric products as the major reaction product can be substantially avoided by employing the sodium or potassium as a fine dispersion. This dispersion is most conveniently made in an inert hydrocarbon or ether as a separate step preliminary to the reaction with the diene.

The reaction medium found most suitable consists essentially of an ether and only certain types of ethers are effective. These particular classes of ethers have the common property of serving as promoters of the diolefin dimerization. The ether can be any aliphatic mono ether having a methoxy group, in which the ratio of the number of oxygen atoms to the number of carbon atoms is not less than 1:4. Examples include dimethyl ether, methyl ethyl ether, methyl n-propyl ether, methyl isopropyl ether, and mixtures of these methyl ethers. Certain aliphatic polyethers are also quite satisfactory. These include the acyclic and cyclic polyethers which are derived by replacing all of the hydroxyl hydrogen atoms of the appropriate polyhydric alcohol by alkyl groups. Typical examples are the ethylene glycol dialkyl ethers such as the dimethyl, methyl ethyl, diethyl, methyl butyl, ethyl butyl, dibutyl, and butyl lauryl ethylene glycol ethers; trimethylene glycol dimethyl ether, glycerol trimethyl ether, glycerol dimethyl ethyl ether, and diethyl-

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ene glycol methyl ethyl ether, dioxane, glycol formal, methyl glycerol formal, and the like, as well as ethyl and methyl ortho formates, methylal and acetals having the proper carbon to oxygen ratio. The simple methyl mono-ethers, as dimethyl ether, and the polyethers of ethylene glycols, as ethylene glycol dimethyl ether are preferred. Hydrocarbon solvents such as isooctane, kerosene, toluene, and benzene cannot be used exclusively as reaction media since they adversely affect the dimerization reaction and give little or no yield of dimer products.

The ethers should not contain any groups such as hy-droxyl, carboxyl and the like which are distinctly re-active towards sodium. Although the ether may react in some reversible manner, it must not be subject to cleavage to give irreversible reaction products during the dimerization process. Such cleavage action destroys the ether and introduces into the reacting system metallic alkoxides which, in turn, tend to induce the rubber form-ing reaction with the diolefin rather than the desired dimerization reaction.

Although the reaction medium should consist essen-tially of the specified ethers other inert media can be employed in limited amounts. In general, these inert media will be introduced with the sodium dispersion as the liquid in which the sodium is suspended. They have the principal effect of diluting the ethers. As the effec-tive concentration of the active ether is decreased by the increased addition of inerts, a minimum concentration of ether is reached below which the promoting effect is not evident. The exact minimum concentration depends up-on the particular reactants and ether being used as well as the reaction conditions, such as temperature, reactant concentration, and the like employed. In any event, the concentration of ether in the reaction mixture should at all times be maintained at a sufficient level to have a sub-stantial promoting effect upon the dimerization reaction. In general, it is good practice to use a reaction medium having at least 50 wt. percent of active ether. Although the amount may be varied considerably, from 100 to 2000 cc. of the ether per mole of diolefin undergoing reaction has been found satisfactory.

It is further necessary to include in the dimerization reaction mixture a relatively small amount of at least one compound of the polycyclic aromatic class. By this term it is intended to include condensed ring hydrocarbons such as naphthalene and phenanthrene, as well as the uncondensed polycyclic compounds such as diphenyl, the terphenyls, dinaphthyl, tetraphenyl ethylene and the like. It is also intended to include mixtures of these compounds. The polyphenyl compounds such as diphenyl and the ter-phenyls and their mixtures have been found to be par-ticularly useful. The amount of the hydrocarbon re-quired will vary over a range which in every case will be relatively small in comparison with the amount of di-olefin undergoing reaction. The exact amount in any particular reaction will depend on temperature, time of reaction and the structure of the diolefin. Concentrations in the range of 0.1 to 10 wt. percent based on the amount of diolefin are ordinarily quite sufficient.

The activation effect which these polycyclic aromatic hydrocarbons show is apparent both in the greatly in-creased selectivity of the diolefin dimerization as well as the increased speed of the reaction.

These active hydrocarbons have the property of yield-ing highly colored sodium hydrocarbon addition prod-ucts in the presence of the active ether employed. While the exact role played by such materials is not fully under-stood and it is not desired to limit the process to an exact theory, they can be regarded as chemical activating agents which, in effect, have the property of transferring metallic sodium to the diolefin in the reaction zone, facilitating its passage through a film of sodium reaction product which would ordinarily effectively isolate the sodium from re-agents present in solution in the surrounding medium. However, the addition of butadiene to an ether solution

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of sodium-terphenyl in the absence of metallic sodium yielded little or no dimerized butadiene products, but only condensed ring products derived from terphenyl. There-fore, this process is not equivalent to the use of a metallic derivative of the polycyclic aromatic compound as the dimerization agent.

It is a further requirement in the process that the re-action temperature preferably be held below 0° C. The temperature range between —20° to —50° C. is the pre-ferred one. Generally speaking, all ethers begin to yield cleavage products at temperatures of about 0° C. and above, with the result that sufficient alkoxides are formed to yield high polymeric acids rather than the desired low molecular weight disodio-diolefin dimers.

The reaction may be carried out in a stirred reaction vessel. In one typical method for carrying out the inven-tion, the sodium or potassium dispersion is initially pre-pared by placing an inert hydrocarbon such as isooctane in a suitable vessel with the appropriate weight of sodium. Using finely dispersed sodium it is only necessary to em-ploy an equimolar amount with the butadiene to be re-acted. Although a slight excess may be added, it is un-necessary and it is desirable to have no unconsumed metal remaining at the end of the reaction period. The mix-ture is heated in a surrounding bath or otherwise until the sodium has melted (M.P. 97.5° C.). Then a suitable high speed agitator is started and, preferably, an emul-sifier consisting, for example, of ½% (based on sodium) of the dimer of linoleic acid is added. After a short period of agitation, a test sample of the dispersion shows the particle size to be in the 5–15 micron range. The stirring is stopped and the dispersion is allowed to cool to room temperature. This dispersion is now ready to be used in the selective dimerization of diolefins. Inert liquids such as saturated dibutyl ether, normal octane, n-heptane, or straight run kerosenes, may be employed as suspension media for the dispersion. Any such disper-sion having sufficiently finely divided sodium or potassium will suffice. Other well-known substances may be used instead of the dimeric linoleic acid as the dispersing agents.

The dispersion is cooled to and maintained below 0° C. and the diolefin introduced either as a gas, or under pressure, in the liquid phase. One quite satisfactory method is to introduce the diolefin into the reaction ves-sel at approximately the same rate as that at which it reacts with the sodium.

This reaction may be carried out either in a batchwise or in a continuous manner and it is not intended to limit the process to any particular method of operation.

The dimetallic derivatives of the diolefin dimers which are selectively formed are thus produced in the reaction mixture. These products, depending on the diolefin, may be either soluble or insoluble in the reaction medium. In general, they tend to form slurries, as for example, the disodiooctadiene produced from sodium and butadi-ene.

It is believed that these dimetallic derivatives are in themselves novel and it is intended to claim them as new compositions of matter. They can either be isolated as such, or, since they tend to be unstable and difficult to handle, they can be directly and immediately thereafter subjected to further reactions to form valuable deriva-tives. For example, subsequent carbonation of the mix-ture containing the products yields the salts of dicar-boxylic acids. The carbonation may be done by sub-jecting the dimetallic-diene derivatives to dry gaseous carbon dioxide, by contact with solid carbon dioxide or by means of a solution of carbon dioxide. The tem-perature should be controlled below 0° C. to avoid the formation of unwanted by-products. This carbonation forms the dimetallic salts of the unsaturated aliphatic dicarboxylic acids. These salts will contain two more carbon atoms than the dimetallic diene dimers from which they are produced. In the case where butadiene

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is the starting aliphatic diolefin, there results by this method the selective production of C_{10} unsaturated dicarboxylic acids.

It is important when producing the diacids and their salts to carry out the dimerization and carbonation as two separate steps. The dimetallic diene dimer is first made and the carbonation is done as soon afterwards as possible. If carbon dioxide is present during the dimerization, the reaction is neither as selective nor as complete.

The diacid salts are water soluble and may easily be separated by a water extraction. Alternatively, they may be converted to the free acids by acidification and separated by filtration, evaporation and/or solvent extraction.

These unsaturated diacid products find use as chemical intermediates, and are valuable in the preparation of polymers and copolymers, plasticizers and drying oils. They are especially useful in esters and polyester and polyamide resins.

In addition, the unsaturated diacids or their salts or other derivatives can be hydrogenated at the double bonds to yield the corresponding saturated compounds, particularly the saturated diacids. This also affords a convenient and accurate way to identify structures of the intermediate products. For example, the disodiooctadiene product obtained from butadiene ultimately yields a practically quantitative mixture of sebacic acid, 2-ethylsuberic acid and 2,2′-diethyladipic acid. Traces of 3-ethylsuberic acid also may be present.

The invention will be described in greater detail by the following examples. These examples and embodiments are illustrative only, and the invention is not in any way intended to be limited thereto except as indicated by the appended claims. All parts are expressed as by weight unless otherwise specified.

EXAMPLE 1

Preparation of C_{10} diacids from butadiene

The reaction was carried out in a stirred reactor having a gas inlet tube extending into the body of the reaction mixture and a reflux condenser vented to a nitrogen atmosphere. This reactor system was purged with nitrogen and charged with 1000 parts of dimethyl ether, 3 parts (about 1.8 wt. percent based on the butadiene used) of para-terphenyl and 69 parts of sodium dispersed in 70 parts of isooctane. The average particle size of the sodium was 15 microns. A stream of gaseous butadiene amounting to a total of 162 parts was passed into the reactor over a 4-hour period while maintaining vigorous agitation and maintaining the reaction temperature at about −25° C. During this period the disodium derivatives of the C_8 butadiene dimers were formed.

After the butadiene addition was completed, the reaction mixture containing the disodium derivatives as a slurry was carbonated by pouring it upon an excess of solid carbon dioxide. After evaporation of excess CO_2, dimethyl ether and isooctane, a solid product, consisting essentially of the sodium salts of the C_{10} unsaturated dicarboxylic acids remained. A small amount, less than 5%, of rubbery butadiene polymer was also isolated. An alkaline solution of the dicarboxylic acids was hydrogenated using a nickel catalyst.

The hydrogenated diacids were precipitated by addition of mineral acid. The combined yield of 10-carbon atom diacids was 67% based on the sodium. Separation and analysis of this mixture showed the following composition:

	Percent
2,2′-diethyladipic acid	8
2-ethylsuberic acid	36
Sebacic acid	23
3-ethylsuberic acid	Trace

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The individual acids were identified by their melting points.

The mixed terphenyls (ortho, meta and para isomers) can be satisfactorily substituted for the para-terphenyl of Example 1. Substantially the same results and products are obtained.

EXAMPLE 2

Preparation of C_{12} diacids from isoprene

Substantially the same procedure as described above in Example 1 was repeated with the exception that 204 parts of isoprene was used as the conjugated diolefin instead of the butadiene. After reaction with finely dispersed sodium followed by carbonation and hydrogenation, the reaction product was found to contain C_{12} dicarboxylic acids in 64% yield based on the sodium.

EXAMPLE 3

Preparation of C_{14} diacids from methyl-pentadienes

A further experiment was carried out following the procedure of Example 1 except that 246 parts of a mixture of 4-methyl-1,3-pentadiene and 2-methyl-1,3-pentadiene was used. The resulting reaction mixture yielded a mixture of C_{14} dicarboxylic acids in 56% yields based on the sodium.

EXAMPLE 4

Preparation of C_{10} diacids using sodium-calcium alloy

The procedure of Example 1 using butadiene was followed except that 75 parts of a sodium-calcium (75:25) alloy was dispersed and used instead of 69 parts of sodium. A yield of 57% of C_{10} dicarboxylic acids based on the sodium was obtained.

EXAMPLE 5

Preparation of C_{10} diacids using sodium-lithium alloy

The same procedure of Example 1 was again repeated using 75 parts of a sodium-lithium (95:5) alloy instead of 69 parts of sodium. This procedure gave a 54% yield of C_{10} dicarboxylic acids based on the sodium.

EXAMPLE 6

Preparation of C_{10} diacids using para-terphenyl

An experiment similar to Example 1 was carried out using substantially the same apparatus as that used in Example 1. The reactor was purged with nitrogen and charged with 320 parts of ethylene glycol diethyl ether and 2 parts of para-terphenyl (about 7.4 wt. percent based on the butadiene used). A dispersion of 25 parts (sodium in 50 parts) of di-n-butyl ether, in which the sodium had an average particle size of 12 microns, was then added. A stream of butadiene totaling 27.1 parts was then passed into the reactor over a period of six hours while maintaining the temperature of the reacting mixture between −25 and −35° C.

After the addition of butadiene was completed, the reaction mixture was carbonated by pouring it onto an excess of crushed Dry Ice. Excess CO_2 was allowed to evaporate and the mixture was treated with about 200 parts of water in a nitrogen atmosphere. The water and hydrocarbon layers were then separated. The oil layer was washed with dilute sodium carbonate solution, which was then added to the water layer. The organic acids were separated from the water layer by acidification with mineral acid. The crude acid so obtained amounted to about 68 parts by weight. This product was dissolved in 200 parts of diethyl ether and hydrogenated over a platinum catalyst to yield the corresponding saturated dicarboxylic acids.

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After hydrogenation, a part of the sebacic acid precipitated from the ether solution. The remaining acid products were isolated by evaporating off the ether solvent, followed by filtration, petroleum ether extraction, and distillation under reduced pressure. The products had the following composition:

	Parts
Sebacic acid	15.8
2-ethylsuberic acid	20.8
3-ethylsuberic acid and 2,2'-diethyladipic acid	4.7

These products represent an 82% yield of C_{10} dicarboxylic acids based on the butadiene.

EXAMPLE 7

Preparation of C_{10} diacids using ortho-terphenyl

An experiment similar in every way to Example 6 was carried out using 2 parts of ortho-terphenyl and 46 parts of dispersed sodium. A yield of 66% of C_{10} dibasic acids was obtained.

EXAMPLE 8

Preparation of C_{10} diacids using naphthalene

An experiment was carried out identical with that of Example 6 except that 2 parts of naphthalene was used instead of para-terphenyl. A 66% yield of C_{10} dicarboxylic acids resulted.

EXAMPLE 9

Preparation of C_{10} diacids using tetraphenyl ethylene

The procedure and conditions of Example 6 were followed using 2 parts of tetraphenyl ethylene instead of para-terphenyl and 46 parts of dispersed sodium. About 10% yield of C_{10} dibasic acids was obtained.

EXAMPLE 10

Preparation of C_{10} diacids using phenanthrene

An experiment similar to that of Example 6 was carried out using 2 parts of phenanthrene instead of para-terphenyl and 46 parts of dispersed sodium. A 51% yield of C_{10} diacids resulted.

EXAMPLE 11

Comparative studies on conditions

A series of comparative experiments was done in a

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critical study of the process. Butadiene was the diolefin employed in all these runs. The details of the operation and the results obtained are shown in the table below.

In runs No. 1 to 4, inclusive, massive bulk sodium metal was used in conjunction with various of the active ethers including both ethylene glycol dimethyl ether and dimethyl ether. The reaction temperature in runs 3 to 8, inclusive, was —25 to —30° C., and about 0° C. in runs 1 and 2. The solid sodium surface was exposed in the reaction mixture throughout the reaction period with the sodium surface being continuously abraded by forcing the sodium piece against a wire brush. In runs No. 1 to 3, inclusive, a separate carbonation step was carried out subsequent to the contacting of the sodium and butadiene, while in run 4, the carbonation was carried out simultaneously. Analysis of the product showed that there was only a trace (a maximum of about 2%) of distillable acids produced. The major part of the butadiene was converted into high molecular weight rubbery products.

Runs 5 and 6 show the results obtained when the process of runs No. 1 through 4 was repeated in the presence of a polycyclic aromatic hydrocarbon, para-terphenyl. The products were found to contain somewhat increased percentages of distillable acids, but, when these were fractionated and studied, they were found to consist largely of high molecular weight acidic products. For example, the result obtained in run No. 5 shows dicarboxylic products of 345 to 540.8 molecular weight (neutralization equivalent×2, assuming diacids). The total yields of these polymeric acids ranged from 53.3% to 56.9%, based on the butadiene. These results clearly show that no selective dimerization has taken place.

The great selectivity and other advantages obtained by using the herein described novel process are obvious from the data of runs 7 and 8. In these reactions finely dispersed sodium (less than 50 microns average particle size) was employed in conjunction with small amounts of the terphenyls as the polycyclic aromatic hydrocarbon. In each case, the reaction was carried out in two steps, the carbonation being separate and distinct. The low neutralization equivalents of the reaction products indicate that they are essentially C_{10} dicarboxylic acids from the carbonation of butadiene dimerization products. An unexpected and superior yield of 80 to 90% based on the butadiene of these low molecular weight diacid products was obtained.

Run No.	Reaction Conditions							Product Analysis		Percent Yield on Butadiene
	Sodium percent excess over theory	Aromatic Hydrocarbon	Solvent	Butadiene		Time, min.	Carbonation Conditions	Distillable acids, gms.	Neut. Equiv.[1]	
				grams	rate					
1	1,000		ethylene glycol dimethyl ether	107	all at start	138	separate step 0.627 g. CO2/min.	trace [2]		
2	1,000		____do____	108	0.5 g./min.	216	separate step Dry Ice	trace [2]		
3	1,000		dimethyl ether	127	0.5 g./ min.	252	____do____	5.4 [2]	142	2.3
4	1,000		____do____	108	0.5 g./min.	250	simultaneous CO2.	5.5 [2]	137	2.5
5	1,000	6 g. para terphenyl (5.8%).	____do____	103	0.37 g./min.	278	separate step Dry Ice	a. 15.1 / b. 46.6 / c. 39.1	172.5 / 152.9 / 270.4	8.0 / 24.6 / 20.7
6	1,000	6 g. para terphenyl (4.2%).	____do____	142	0.63 g./min.	226	____do____	a. 13.2 / b. 45.2 / c. 84.0	397.2 / 207.0 / 511.7	5.3 / 18.0 / 33.6
7	[3]50	ortho-terphenyl	____do____	27	0.1 g./min.	300	____do____	44.5	107	90
8	[3]120	para-terphenyl.	____do____	27	0.1 g./min.	300	____do____	40.6	111	83

[1] The theoretical neutralization equivalent for C_{10} dibasic acids is 101, and the molecular weight is 202.
[2] The major product from the butadiene was white, polymeric rubber acids.
[3] Dispersed Na.

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EXAMPLE 12

Attempted use of sodium-terphenyl complex

The reaction of butadiene with a sodium-terphenyl complex was attempted. The results obtained indicate that, in the absence of metallic sodium, only unwanted by-products were formed, and no detectable dimerization of butadiene occurred.

A solution of 115 grams (0.5 mole) of ortho-terphenyl in 525 cc. of the diethyl ether of ethylene glycol was contacted with sodium ribbon (99 g., an excess) for a period of time. The resulting solution was decanted from the excess metallic sodium. Analysis by titration indicated that approximately 0.68 mole of sodium had combined with the 0.5 mole of ortho-terphenyl.

This ortho-terphenyl-sodium solution was diluted with an additional 150 cc. of the diethyl ether of ethylene glycol. Butadiene (0.68 moles) was then passed into this diluted mixture over a three-hour period at a temperature of −30° C. The clear solution obtained after centrifuging was distilled to give 45 g. of a solid. The original solid was carbonated, then treated with water and free acid. Less than 0.5 g. of organic acids was obtained. An extraction with dibutyl ether gave a large amount of a crystalline solid. The total amount of solids obtained was equivalent to a practically theoretical yield of non-acid material consisting substantially of triphenylene; M.P. after recrystallization, 197–199° C.; M.P. of picrate, 222–224° C.; literature values, 198.5° and 223°, respectively.

From the above experiment, it is clear that the butadiene did not undergo the desired dimerization reaction in the presence of the sodium containing complex. It is evident that the presence of the alkali metal is essential for the selective dimerization of the conjugated diolefins as herein described.

As is apparent from the aforesaid description of the invention, the compositions produced by the defined selective dimerization reaction between the alkali metal and conjugated aliphatic diolefin comprise a mixture of selectively formed dialkali metal dimers of the diolefin and which dimer products are composed, in a major part by weight, that is, more than 50% by weight, of the dimer mixture, of branched-chain dimers, with the remainder being a straight chain dimer, and the diacid products prepared by carbonation of the selectively formed dialkali metal dimer mixture to form salts having two more carbon atoms per molecule than a dimer of the diolefin, as well as the diacids liberated from their salts, also result in mixtures in which the major amount by weight, that is, more than 50% by weight, is composed of branched-chain components and a minor amount by weight, that is, less than 50% by weight, of a straight chain component. Thus, as aforedisclosed, and illustrated by use of butadiene as the diolefin reactant, there is ultimately produced after carbonation and hydogenation, from the selective dimerization process, a mixture of C_{10} aliphatic saturated diacids composed substantially of sebacic acid; α,α'-diethyladipic acid; and α-ethylsuberic acid in a ratio, by weight, of about 33:12:54, respectively, or expressed otherwise, about ⅓ part of sebacic acid and about ⅔ part of the branched chain C_{10} aliphatic saturated diacids.

The aforedescribed mixtures of dialkali metal derivatives of the selectively dimerized aliphatic conjugated diolefins are novel mixtures useful as chemical intermediates from which can be prepared novel mixtures of diacids from which can be prepared polyamide resins, polyesters, ester plasticizers, and other products, and, in general, for preparation of derivatives requiring use of a diacid component. Examples of usefulness of the mixtures of the dialkali metal derivatives of the selectively dimerized diolefin include (1) reactions with a compound capable of metallation such as butenes, toluene, and the like to produce metallated derivatives which can in turn be

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subjected to further reactions such as carbonation, (2) reactions with an epoxide such as ethylene oxide, followed by hydrolysis, to prepare glycols, (3) reactions with carbonyl compounds such as aldehydes and ketones such as formaldehyde and acetaldehyde, followed by hydrolysis, to prepare glycols, (4) reactions with oxygen to prepare unsaturated glycols which can be hydrogenated to saturated glycols, and (5) reactions with haloaliphatic ethers to prepare dialkoxy derivatives that can be hydrogenated and oxidized to dibasic acids.

The unsaturated diacid products of the carbonation step, that is, the dialkali metal salts of the unsaturated diacids, having two more than the number of carbon atoms in the dimers, can be (1) reacted with alkyl halides to produce unsaturated esters, (2) reacted with hydrogen peroxide or other peroxides in aqueous solution to produce glycols, (3) reacted with oxygen to produce mixtures of oxidation products such as acids, and aldehydes, (4) specific salts such as the initially prepared sodium salts can be reacted with a compound such as lithium hydroxide for interconversion to the corresponding lithium salts, and (5) with substances such as bromine, hydrogen bromide, and the like to form addition products at the unsaturated bonds.

With reference to the mixtures of saturated aliphatic diacids prepared by the aforedescribed method and which mixtures contain, in major amount, branched-chain diacids, such mixtures possess properties whereby they are useful in preparation of dialkyl esters, mixed dialkyl esters, polyesters, and polyamides. Many of these products, for instance the esters and the polyamides, possess characteristics that are unobvious when compared to corresponding products using diacids other than the novel mixtures embodied herein. For example, with reference to diacid mixtures embodied herein and prepared by use of butadiene for the selective dimerization reaction, there is prepared the aforedescribed mixture of C_{10} aliphatic saturated diacids composed substantially of sebacic acid, α-ethylsuberic acid and α,α'-diethyladipic acid, with the sums of the latter two acids comprising the major amount by weight, that is, more than 50% by weight, of the saturated C_{10} diacid mixture. Such mixtures, per se, or those from which some of the sebacic acid, the linear isomer, is removed thereby providing a mixture containing all three of the components but having still higher proportional amounts of the branched chain diacids, that is, containing at least 80% by weight, or a still higher percentage on the order of at least about 85%, are useful for reaction with suitable diamines to prepare polyamides that not only are fiber-forming but possess clarity characteristics not obtainable by use of sebacic acid per se as the diacid for the polyamide resin formation. For example, whereas prior art disclosures disclose that fiber-forming polyamides prepared from sebacic acid and hexamethylenediamine are opaque, whereas clear polyamides can be prepared by use of the aforesaid isomeric mixture of C_{10} diacids as the diacid component for the polyamide formation.

Also it has been found that such mixtures per se, or those from which some of the sebacic acid is removed giving the mixtures aforedescribed having higher proportional amounts of the branched-chain diacids, are useful for preparation of diesters and polyesters, by reaction with glycols under polyester-forming conditions, the diesters having improved and unexpected properties as plasticizers which are not obtainable by use of esters of any of the individual component acids, nor from esters prepared from closely related homologs and isomers. These improved plasticizer properties include excellent low temperature characteristics, high plasticizer efficiency, and good oil extraction and migration properties. While the mixed esters can be used in many types of resins as plasticizers, they find particular importance in vinyl resins, such as polyvinyl chloride polymers, vinyl chloride-vinyl acetate polymers, polyvinyl acetals,

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and polyvinylidene chloride, in proportions of from 5 to 100 parts of ester per 100 parts of resin.

The combination of unusually excellent properties as aforedescribed and obtained by use of the alkyl esters of these diacid mixtures are unexpected and permit using these materials as plasticizers in resins to obtain compositions having highly desirable characteristics not obtainable by use of ester plasticizers from other diacids.

What is claimed is:

1. A mixture consisting essentially of sebacic acid, α-ethylsuberic acid and α,α'-diethyladipic acid, at least two-thirds of said mixture being comprised of the two branched chain acids the remainder being sebacic acid.

2. An isomeric mixture consisting essentially of disodium diolefinic aliphatic dimers of a conjugated aliphatic diolefin having from 4 to 8, inclusive, carbon atoms

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per molecule, at least a major portion of more than 50% of said isomeric mixture being comprised of at least two different branched chain isomers the remainder being the straight chain isomer.

3. An isomeric mixture consisting essentially of disodium diolefinic dimers of butadiene, at least a major portion of more than 50% of said isomeric mixture being comprised of at least two different branched chain isomers each of which has at least one C_2 branch per molecule the remainder being the straight chain isomer.

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