[CONTRIBUTION FROM THE RESEARCH DIVISION, U. S. INDUSTRIAL CHEMICALS CO. AND APPLIED SCIENCE RESEARCH LABORATORY, UNIVERSITY OF CINCINNATI]

New Synthesis of Dibasic Acids[1-3]

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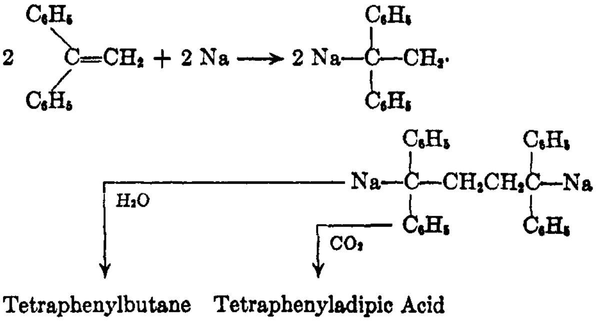
A new organometallic compound, disodiooctadiene, has been synthesized by the reaction of butadiene and sodium. This product by reaction with carbon dioxide yields a new family of unsaturated 10-carbon dibasic acids, which in turn may be hydrogenated to the saturated dibasic acids, sebacic, 2-ethylsuberic, and 2,5-diethyladipic acids.

Alkali metals may react with unsaturated hydrocarbons in a number of ways depending upon the metal, the hydrocarbon and the reaction conditions. The major types of reaction are addition, additive dimerization, and polymerization. The present paper is concerned with the extension of the additive dimerization reaction to afford a new synthetic route to a variety of difunctional compounds. It is of interest to discuss briefly these general reaction types to show the new development in relation to previous observations in this field.

In general, simple addition reactions have been limited to polycyclic hydrocarbons such as naphthalene and anthracene[5] or to highly substituted ethylenes such as 1,2-diphenylethylene.[6] However, it has been reported that the very strongly electropositive metal, cesium, can add to ethylene itself.[7] It thus appears that simple addition occurs most readily with the more highly conjugated hydrocarbons, and that it is also favored by an increase in the electropositive nature of the metal. Addition of sodium or potassium to simple olefins has never been reported.

In the presence of a suitable hydrogen donor, the reaction of alkali metal with unsaturated hydrocarbons may result in hydrogenation. This reaction is of broader scope than the simple metal addition, since it is applicable not only to the condensed cyclic hydrocarbons and highly substituted ethylenes,[8] but also to styrene[9] and to simple *alpha*-olefins.[10] Thus far it has not been possible to reduce *beta*-olefins in this manner.

With hydrocarbons which yield a suitably stabilized monoalkali metal adduct, reaction with an alkali metal results in an additive dimerization. This was first observed by Schlenk in 1914 with 1,1-diphenylethylene,[11] and subsequently was extended to a variety of di- and trisubstituted ethylenes by Schlenk, Ziegler, Conant, and others.[12] However, efforts to effect this reaction with simpler substituted ethylenes such as styrene and butadiene yielded polymer.



While unsuccessful in accomplishing metalative dimerization of the simpler substituted ethylenes, previous workers have reductively dimerized certain of these unsaturated hydrocarbons to yield the corresponding dihydro product. For example, isoprene has been treated with potassium in alcohol to yield a mixture of isomeric decadienes.[13] Similarly, butadiene with sodium in liquid ammonia has been observed to produce a low yield of octadiene.[14] As in simple addition to unsaturated hydrocarbons, dimerization in the presence of a hydrogen donor is of broader scope than metalative dimerization.

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[1] Abstracted from the thesis of W. E. Foster submitted in partial fulfillment of the requirements for the Ph.D. degree to the University of Cincinnati.

[2] This work was carried out under a Fellowship supported by the U. S. Industrial Chemicals Company at the Applied Science Research Laboratory of the University of Cincinnati. Certain phases of the study were completed at the Research Division of the sponsoring company, and advances in a better understanding of the reaction have resulted from the contributions of V. L. Hansley, J. F. Nobis, S. Schott, and others in that laboratory. For assistance in preparation of this paper the authors are particularly indebted to J. Feldman (separation of reaction products and resolution of diethyladipic acid) and F. Miller (determination of physical properties of the dibasic acids).

[3] Presented before Division of Industrial and Engineering Chemistry, 133rd Meeting, ACS, San Francisco, Calif., April 1958.

[4] Present address: Ethyl Corporation, Baton Rouge, La.

[5] C. S. Rondestvedt and I. Nicholson, *J. Org. Chem.*, **20**, 346 (1955).

[6] A. G. Brook, H. L. Cohen, and G. F. Wright, *J. Org. Chem.*, **18**, 447 (1953).

[7] L. Hackspill and R. Rohmer, *Compt. rend.*, **217**, 152 (1943).

[8] A. Klages, *Ber.*, **35**, 2646 (1902).

[9] K. Ziegler *et al.*, *Ann.*, **511**, 64 (1934).

[10] H. Greenfield, R. A. Friedel, and M. Orchin, *J. Am. Chem. Soc.*, **76**, 1258 (1954).

[11] W. Schlenk *et al.*, *Ber.*, **47**, 473 (1914).

[12] K. N. Campbell and B. K. Campbell, *Chem. Rev.*, **31**, 77 (1942).

[13] T. Midgley and A. L. Henne, *J. Am. Chem. Soc.*, **51**, 1293 (1929).

[14] W. Huckel, and H. Bretschneider, *Ann.*, **540**, 157 (1939).

Thus, hydrocarbons which yield dimetallo dimers also yield the dihydro dimer if reaction occurs in the presence of a suitable hydrogen donor.

Attempts also have been made to employ reactants other than active hydrogen compounds to block the sodium-diene reaction at the dimer stage. One of these was the work of Walker who fed a continuous stream of carbon dioxide through the reaction mixture while abrading a block of sodium in the presence of an ether solution of butadiene.[15] Walker's product was a mixture of unsaturated, polymeric acids which was not separated or characterized further.

The third general type of reaction is polymerization. Those hydrocarbons which most readily add metal or are readily dimerized, show little or no tendency to polymerize. The symmetrical and unsymmetrical diphenylethylenes are the classic examples of these types. In these compounds, the initial monosodium adduct has too much resonance stabilization and/or steric interference to permit the propagation of a polymerization step. On the other hand, styrene is one of the most readily polymerized monomers in view of its reactivity toward an electropositive material such as sodium, and the readiness of chain propagation. Aliphatic dienes are only slightly less reactive toward alkali metals, and as a result polymerization is the most common reaction of styrene[12] or of an aliphatic diene[16,17] with an alkali metal.

In reviewing these reaction types it became apparent that if one could suppress the polymerization of compounds such as butadiene and styrene, it should be possible to accomplish a metalative dimerization which then would make available an extremely powerful tool for the synthesis of a variety of difunctional compounds. A further piece of evidence appeared in 1951 when a very interesting paper was published by the late Dr. M. S. Kharasch reporting the dimerization of butadiene by means of *t*-butoxy radicals to obtain the dibutyl ether of octadienediol.[18] In this work, a 70% yield of the normal product and 17% of the branched product were obtained by the reaction of butadiene and *t*-butyl hydroperoxide employing ferrous ion as the peroxide activator at −10 to −20°.

$$t\text{-BuOOH} + \text{Fe}^{++} \longrightarrow t\text{-BuO}\cdot + \text{OH}^- + \text{Fe}^{+++}$$

$$t\text{-BuO}\cdot + \text{CH}_2\text{=CHCH=CH}_2 \longrightarrow t\text{-BuO—CH}_2\text{CH=CHCH}_2\cdot$$

$$2\ t\text{-BuO—CH}_2\text{CH=CHCH}_2\cdot \longrightarrow t\text{-BuO—(CH}_2\text{CH=CHCH}_2)_2\text{—OBu}$$

This work strengthened the belief that a similar coupling could be effected with sodium, providing (a) the sodium would be supplied to the butadiene in a "solubilized" form, and (b) reaction conditions were employed which favored dimerization rather than polymerization. Kharasch's temperature and reaction conditions suggested a general answer to the second requirement; after some investigation, an answer to the first requirement was found to be in the use of finely dispersed sodium, a sodium "carrier," and an "active ether medium."[19]

The first successful reaction was carried out employing tetraphenylethylene as the "carrier" and ethylene glycol diethyl ether as the medium; while the yield was low in this initial run, the search for better "carriers" quickly developed a procedure with yields of 10-carbon dibasic acids as high as 90% on the butadiene.[20]

The function of the "active" ether is analogous to the role of ether in the Grignard reaction, *i.e.*, to facilitate the formation of the organometallic compound through association as an ether complex. Particularly effective ethers include the dimethyl ether and diethyl ether of ethylene glycol, dimethyl ether, and tetrahydrofuran. The promoting effect of these ethers also has been observed in other alkali metal reactions, for example, the formation of sodium-naphthalene addition compounds,[19] reactions with other aromatic hydrocarbons,[21] and in various metal halide reductions.[22] The "carrier" itself presumably "solubilizes" an atom of sodium as a loose organosodium compound and it, in turn, passes on the sodium to the butadiene where the irreversible formation of disodiooctadiene occurs.

The most serious side reaction in the butadiene coupling process is the formation of polymer. The rigid exclusion of reactive substances such as water, alcohols, and carbon dioxide is a primary requisite to suppress this polymerization tendency. A second side reaction which may prove troublesome is metalation of reactive C—H bonds by disodiooctadiene. This may occur during the initial coupling step provided sufficiently reactive compounds are present. In such a case, two monobasic acids will be formed on carbonation. On the other hand, carbonation of the disodioctadiene with too limited a supply of carbon dioxide also will result in loss of product through metalation side reactions. In this case, product formed at the start of the carbonation will be metalated by disodiooctadiene still present in the reaction mixture. This type of side reaction during the carbonation step has been observed previously[23,24,25] and results in the formation of malonic

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[15] J. F. Walker, U. S. Patent **2,352,461** (6/27/44).

[16] K. Ziegler *et al.*, *Z. Angew. Chem.*, **49**, 499 (1936); *Ann.* **567**, 72 (1950).

[17] F. W. Stavely *et al.*, *Ind. Eng. Chem.*, **48**, 778 (1956).

[18] M. S. Kharasch, F. S. Arimoto, and W. J. Nudenberg, *J. Org. Chem.*, **16**, 1556 (1951).

[19] N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Am. Chem. Soc.*, **58**, 2442 (1936).

[20] C. E. Frank and W. E. Foster, French Patent **1,093,-096** April 29, 1955), U. S. Patent **2,816,916** (Dec. 17, 1957).

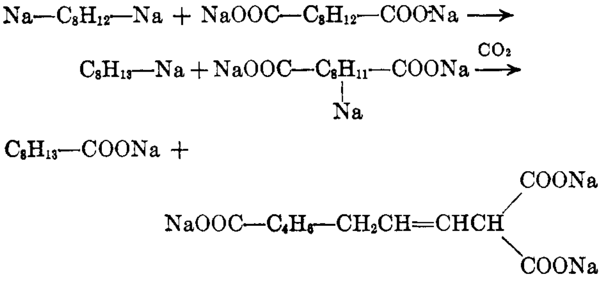
[21] D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

[22] J. L. Down *et al.*, *Proc. Chem. Soc., July*, 1957, 209.

[23] A. A. Morton, F. Fallwell, and L. Palmer, *J. Am. Chem. Soc.*, **60**, 1426 (1938).

[24] H. Gilman and H. A. Pacevitz, *J. Am. Chem. Soc.*, **62**, 1301 (1940).

acids. With disodiooctadiene, monobasic and tribasic acids will result:



$$Na—C_8H_{12}—Na + NaOOC—C_8H_{12}—COONa \longrightarrow C_8H_{13}—Na + NaOOC—\underset{\substack{|\\Na}}{C_8H_{11}}—COONa \xrightarrow{CO_2} C_8H_{13}—COONa + NaOOC—C_4H_6—CH_2CH=CHCH(COONa)_2$$

Here, metalation would be particularly easy because of the additional activation of the *alpha*-methylene group by the allylic double bond.

The occurrence of these reactions is evidenced by the presence of monobasic acids in all products prepared by this synthesis. While these amounts of monobasic acids formed under optimum conditions may amount to only 1–2%, the fact that they are always present suggests that a certain amount of *trans*-metalation and cleavage of the ether medium always occurs. Tetrahydrofuran and the glycol ethers are more subject to this type attack than is dimethyl ether.

By analogy with other dimerization reactions, there is little doubt that the reaction sequence is as follows:

$$CH_2=CHCH=CH_2 + Na \longrightarrow \overset{+}{Na}\,\overset{-}{C}H_2CH=CHCH_2\cdot$$

$$2\ \overset{+}{Na}_2\overset{-}{C}H_2CH=CHCH_2\cdot \longrightarrow \overset{+}{Na}\,\overset{-}{C}H_2CH=CHCH_2CH_2CH=CH\overset{-}{C}H_2\overset{+}{Na}$$

Disodiooctadiene is written as a largely electrovalent compound, which is consistent with the properties of other aliphatic organosodium compounds. If this is correct, then the divalent octadiene anion would have several limiting forms including those with reactive points allylic to the terminal position:

$$[\overset{-}{C}H_2CH=CHCH_2CH_2CH=CH\overset{-}{C}H_2]$$

$$[CH_2=CH\underset{-}{C}HCH_2CH_2CH=CH\overset{-}{C}H_2]$$

$$[CH_2=CH\underset{-}{C}HCH_2CH_2\underset{-}{C}HCH=CH_2]$$

It would be expected that carbonation and hydrogenation of the resultant unsaturated acids should yield three major products—sebacic acid, 2-ethylsuberic acid, and 2,5-diethyladipic acid. This was found to be the case with the three products indicated occurring in the ratio of 3.5:5:1, respectively. This represents a ratio of primary to secondary in the disodiooctadiene resonance hybrid of approximately 12:7.

It is interesting to note that the dominance of primary over secondary product also is borne out in the monobasic acids. However, the ratio of pelargonic to 2-ethylheptanoic is somewhat greater (3:1) than would be calculated from the composition of dibasic acids. If the accuracy of these figures is confirmed, it would indicate a greater reactivity (*i.e.*, loss to metalation side reactions) of the secondary than the primary position.

Carbonation of disodiooctadiene yields as the initial product a mixture of new unsaturated ten-carbon, dibasic acids comprising 3,7-decadienedioic acid, 2-vinyl-5-octenoic acid, and 2,5-divinyladipic acid. A discussion of the properties of the unsaturated 10 carbon dibasic acids and their applications is contained in a forthcoming publication. These products are of considerable interest in the formation of novel alkyd and polyester coating compositions and in selected copolymerizations.

Until the development of the present synthesis, 2-ethylsuberic and 2,5-diethyladipic acids were little known compounds. The diethyladipic appears to have been synthesized only once before, that being by the decarboxylation of 3,3,6,6-octane-tetracarboxylic acid.[26] This product contains both the racemic and meso isomers; the racemic form has been resolved by recrystallization of the brucine salts.

2-Ethylsuberic acid has been prepared previously by the decarboxylation of 2-ethyl-2-carboxy-1,8-octanedioic acid.[27,28] This product is intermediate in solubility between the very soluble racemic diethyladipic and the slightly soluble sebacic and meso-diethyladipic acids.

Major commercial interest in this synthesis lies in the saturated dibasic acid product comprising approximately 51% 2-ethylsuberic, 38% sebacic, and 11% 2,5-diethyladipic. This mixture may be sold as such ("USI-DDA"), or it may be separated by fractional crystallization[29] into sebacic and "Isosebacic" acids, the latter comprising 72–80% 2-ethylsuberic, 12–18% diethyladipic, and 5–10% sebacic.

It is apparent that this metalative dimerization reaction affords an extremely versatile and useful new synthetic method. Thus, other aliphatic dienes in addition to butadiene may be converted to dibasic acids through the disodio dimer derivative. Isoprene and 1,3-pentadiene for example yield mixtures of 12-carbon dibasic acids, the increased number of isomers resulting in increasingly complex mixtures.[20] By similar procedures, styrene also can be dimerized in good yields to 2,5-diphenyladipic acid; this is described in an accompanying publication [*J. Org. Chem.*, **26,** 307 (1961)].

Extension of the synthesis also can be accomplished by condensing the organosodium inter-

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[25] J. F. Nobis and L. F. Moormeier, *Ind. Eng. Chem.*, **46,** 539 (1954).

[26] B. Lean, *J. Chem. Soc.*, **65,** 1009 (1894).

[27] B. R. Baker *et al.*, *J. Org. Chem.*, **12,** 186 (1947).

[28] W. Keil, G. Schuller, *Z. physiol. Chem.*, **282,** 135 (1947); C. A. **43,** 6164 (1949).

[29] S. A. Mednick, R. Wynkoop, J. Feldman, U. S. Patent 2,858,337 (Oct. 28, 1958).

PHYSICAL PROPERTIES OF THE 10-CARBON DIBASIC ACIDS

Properties	2,5-Diethyladipic	2-Ethylsuberic	Sebacic
M.p.	72–73 (racemic) 138–139 (*meso*)	77.5–78.5	134.5
B.p. 760 mm. (calcd.)	332.8	338.6	349.1
B.p., 1 mm.	174.1	182.4	189.3
dt/dP at 1 mm., °C./mm.	16.4	17.1	17.4
Latent heat of vaporization at 1 mm., cal./g.	120	119	120
Density at 140° g./ml.	0.9779 (*meso*)	0.9832	0.9861
dD/dt	0.000733 (140–190°)	0.000691 (80–130°)	0.000727 (140–190°)
Coefficient of expansion/°C.	0.000764 (140–190°)	0.000686 (80–130°)	0.000751 (140–190°)

mediates with reactants other than carbon dioxide. Reaction of disodiooctadiene with oxygen, formaldehyde or ethylene oxide, for example, yields the eight, ten, and twelve carbon glycols[30-32]; these products will be described in a future publication. Other reactions still under investigation also will be reported at a later date.

EXPERIMENTAL

A 2-l., three necked flask was fitted with a gas-inlet tube, an efficient stirrer, a Dry Ice–cooled condenser and a thermometer reaching below the surface of the liquid. The apparatus was purged with nitrogen, and a nitrogen blanket maintained throughout the reaction. Ethylene glycol diethyl ether (800 cc.) and 3 g. of *p*-terphenyl were added to the flask, and the mixture was stirred a few minutes to dissolve the terphenyl. All ether used in this work should be carefully purified, *e.g*, by fractional distillation followed by a second distillation from sodium-benzophenone complex. The sodium dispersion comprising 100 g. of a 50% dispersion of sodium (2.2 g.-atoms) in a refined kerosene was added to the flask under an atmosphere of nitrogen. The particular dispersion in the example had an average particle size of 10–12 microns and was prepared by the conventional high speed stirring procedure[33]; the dispersing aid was 0.5% of "dimer acid" (dimerized linoleic acid). An intense blue color of the sodium-terphenyl complex developed on adding the sodium dispersion to the ether solution. If the color does not develop, it is an indication of excessive contamination and the desired coupling will not occur.

The flask was cooled to about −30°, and, with good agitation, 54 g. (1 mole) of butadiene was passed in over a period of about 4 hr. This was conveniently accomplished by entraining in a metered stream of nitrogen which was bubbled through a flask of liquid butadiene held at −20°. During the butadiene addition the reaction mixture retained a deep blue color, although there was a change in shade from the original sodium-terphenyl color. Colors of some of the other more effective carrier-sodium adducts are *o*-terphenyl-deep brown, naphthalene-green, diphenyl-blue.

At the conclusion of the reaction, the mixture was poured with stirring onto a large excess of crushed Dry Ice in a stainless steel beaker; the nitrogen blanket was maintained on the mixture throughout this operation. It should be noted that disodiooctadiene is a highly pyrophoric material, and that combinations with flammable solvents should be handled with extreme care. While reactions carried out in ethylene glycol ethers may be handled as described, it is recommended that any such work in dimethyl ether (boiling point, −23°) be conducted in all metal equipment, and that the disodiooctadiene slurry be transported through metal tubing from one vessel to another under nitrogen pressure; *a slurry of disodiooctadiene in dimethyl ether is an extremely hazardous mixture.*

The excess Dry Ice was allowed to evaporate by standing in the hood over night; unchanged sodium in the carbonated product was then quenched by the cautious addition of 200 cc. of water over a 0.5-hr. period. The operation should be kept blanketed by nitrogen or carbon dioxide to prevent ignition of the solvent by sparks from the reacting sodium. After addition of the water, the mixture was essentially colorless and contained a heavy, white precipitate. This was transferred to a 2-l. separatory funnel where another 400–500 cc. of water was added to give complete solution. The clear, yellow, aqueous layer which separated from the organic solvent contained almost all the acidic material as sodium salts. This was made acid to Congo Red using concentrated hydrochloric acid; the acid separated as a yellow oil which was removed completely from the aqueous layer by extraction with four 100-cc. portions of ether. The ether solution was hydrogenated in a Parr hydrogenator at about 40 lbs./sq. in. pressure using Adams' platinum oxide catalyst. Under these conditions a portion of the sebacic acid precipitated and may cover up the catalyst thereby preventing complete hydrogenation. In any event, the product should be checked for unsaturation before proceeding to the separation and purification step, as relatively small amounts of residual unsaturated acids will retard crystallization and iso-

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(30) C. E. Frank and J. F. Nobis, U. S. Patent 2,850,540 (Sept. 2, 1958).

(31) S. Schott and E. A. Allgeier, Brit. Patent 780,205 (July 31, 1957).

(32) J. F. Nobis and E. A. Allgeier, Brit. Patent 778,924 (July 17, 1957).

(33) The dispersions used throughout this basic work were prepared by high speed stirring of molten sodium in hydrocarbon or dibutyl ether medium containing 0.5% of a dispersing agent. [*Ind. Eng. Chem.*, **45**, 404 (1953)]. Such dispersions had an average particle size in the range of 10–15 microns. The use of these dispersions in a typical reaction as described above required about 100% excess sodium to obtain efficient dimerization of the butadiene. As would be expected, subsequent work showed that much increased sodium efficiency could be realized by employing attrition during the reaction (U. S. Patent 2,816,917) or the use of extremely fine dispersions (U. S. Patent 2,816,936). An unexpected result in these latter instances was the finding that the "carrier" was not necessary if extremely fine sodium were supplied to the reaction. Thus, it is possible to effect a "mechanical activation" of the sodium by attrition or by the preparation of submicron dispersions which is comparable in its results to the "chemical activation" brought about by the sodium "carrier."

lation of the final products. In larger runs it may be more convenient to hydrogenate the aqueous solution of sodium salts using a nickel catalyst and several hundred pounds hydrogen pressure.

The ether and any residual water were removed by evaporation at reduced pressure to yield 90 g. of crude acids. These were dissolved in 100 cc. of hot toluene, and the hot solution was treated with carbon black and filtered. On cooling to room temperature, the sebacic acid separated as a beautiful white crystalline product, m.p. 131.5–132.5°; 30 g. (30% based on butadiene). The remaining acids comprise a complex mixture from which the individual isomers cannot be separated in good yields by any simple procedure. Thus, some of the sebacic remains associated with the ethylsuberic and cannot be directly crystallized despite the large difference in solubility. Another difficulty arises from the fact that most of the diethyladipic is present as the very soluble, racemic isomer. The following procedure comprises the most suitable laboratory separation:

An additional 50 cc. of toluene was added to the filtrate from the sebacic acid crystallization. This solution was then agitated for 2 hr. with a mixture of 10 cc. of water and 50 g. of urea at 30°. The mixture was filtered and the solid washed with small volumes of toluene. The solid urea–sebacic acid adduct was decomposed by warming with 100 cc. of water and filtering the urea solution from the liberated sebacic acid; 7 g. of additional sebacic acid was recovered in this manner.

The original filtrate from the adduction comprises a toluene phase containing diethyladipic acid and a heavy oily phase which is the salt of urea and ethylsuberic acid. This salt phase was separated from the toluene solution and decomposed by carefully adding 100 cc. of 80% sulfuric acid. The crude ethylsuberic acid was removed by filtration and dried (weight = 42 g.); it was recrystallized from 150 cc. of toluene at 5° to yield 35 g. of acid, m.p. 75–77°.

It is difficult to recover racemic diethyladipic acid from toluene solution since other acids present at this stage interfere with its crystallization. Small yields may be obtained by crystallization at 0° from a mixture of toluene and hexane and then recrystallized from anhydrous acetonitrile at 0° to give the pure compound. However, a more effective acid separation is obtained by first converting the racemic to the *dl*-*meso*-mixture and crystallizing the *meso* acid. In the present example, racemization of the diethyladipic acid was affected by distilling the toluene from the acids, then heating the acids under nitrogen at 250° for 1.5 hr. Pure *meso*-diethyladipic acid (5 g.) was obtained by crystallization from 30 cc. of toluene; m.p. 138–139°.

The filtrate at this point is largely racemic diethyladipic acid with small amounts of ethylsuberic and sebacic acids, and of monobasic acids resulting from transmetalation side reactions. Such residues from a number of runs were combined and the racemic diethyladipic isolated by recrystallization from acetonitrile; m.p., 72–73°. This acid was resolved by recrystallization of the brucine salts; $[\alpha]^{25}_{D} = \pm 19°$; m.p., 76–77°. Racemic diethyladipic is quite soluble in water and in most organic solvents in contrast to the *meso* acid which resembles sebacic in its general solubility behavior.

After removal of acetonitrile from the filtrate the small remaining residue was distilled at reduced pressure. Small amounts of pelargonic acid (b.p. 130°/8 mm.) and α-ethylheptanoic acid (b.p. 123°/8 mm.) amounting to approximately 1% and 0.5% of the total product were isolated[34] and identified as the piperazonium salts (m.p., 95–96° and 69–70°, respectively).

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[34] F. M. Trent, F. D. Miller, and G. H. Brown, *Chem. Eng. Data*, 5, 110 (1960).

[CONTRIBUTION FROM THE RESEARCH DIVISION, U.S. INDUSTRIAL CHEMICALS CO.]

A New Synthesis of Dibasic Acids. II.
2,5-Diphenyladipic Acid and Related Compounds[1]

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2,5-Diphenyladipic acid and 2,5-dimethyl-2,5-diphenyladipic acid have been synthesized by the metalative dimerization of styrene and α-methylstyrene, respectively, with sodium and subsequent reaction with carbon dioxide.

The first paper in this series[3] reports the discovery of a new synthesis of dibasic acids involving the metalative dimerization of conjugated dienes to obtain the dimetallo dimer followed by carbonation. The present paper is concerned with the extension of this reaction to styrene and substituted styrenes to yield dibasic acids containing aromatic substituents on the carbon chain. The more important of these products are 2,5-diphenyladipic acid and 2,5-dimethyl-2,5-diphenyladipic acid obtained by the metalative dimerization of styrene and of α-methylstyrene, respectively. 2,5-Diphenyladipic acid has been reported only once previously and was obtained *via* the malonic ester synthesis through 2,5-dicarboxy-2,5-diphenyladipic acid.[4] 2,5-Dimethyl-2,5-diphenyladipic acid is a new product, of special interest because of the absence of any *alpha* hydrogen atoms. Both diphenyladipic and dimethyldiphenyladipic acids are readily converted

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[1] The work was initiated under a Fellowship supported by the U.S. Industrial Chemicals Company at the Applied Science Research Laboratory of the University of Cincinnati. Development of the reaction and synthesis of the various derivatives were conducted at the Research Division of the sponsoring company.

[2] Present address: Metal & Thermit Corporation, Rahway. N. J.

[3] C. E. Frank and W. E. Foster, *J. Org. Chem.*, 26, 303 (1961).

[4] S. M. McElvain and P. M. Laughton, *J. Am. Chem. Soc.*, 73, 448 (1951).