execution of such a plan are to be found in the already published first and third volumes of his "*Method for the Identification of Pure Organic Compounds.*" All that is desired here is to lead to a discussion of the advantages in the plan for Chemistry; and, if it is sound, to arouse interest with a view to eventually bringing about a wider coöperation for furthering its future development. The difficulties to be overcome are considerable. Recorded descriptions of organic compounds, while frequently very complete for a few properties like melting and boiling points, are commonly equally deficient concerning others—especially in exact data showing the extent of the influence of slight variations in chemical constitution on the results of the selected differential tests. The occasion hence arises for an investigation or partial reexamination of a considerable proportion of the species receiving locations. If one has the pure compounds with which to experiment, the tests are easily made. But as only a few thousand pure compounds can be procured through commercial channels, and most of these require some purification, success in the construction of a comprehensive diagnostic classification implies assistance from private collections throughout the world; for to synthesize any considerable part of the rarer species would overtax the facilities of the largest and best equipped of laboratories.

To bring a majority of the carbon compounds referred to in Richter's Lexikon into an essentially "natural" classification of the kind suggested would, assuming the study of tests and revision of constants to be thoroughly done, perhaps involve a labor as great as the transformation of the "artificial" botanical classification of Linnaeus into the modern "natural" system as it was left by de Candolle. An undertaking of this magnitude and character might presumably in the present century be accomplished with greater benefit to science under the direction of some such organization as the committee entrusted with the periodical revision of Beilstein's "Handbuch" and the Richter "Lexikon" than under private auspices.

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[CONTRIBUTION FOR THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

SYNTHESIS OF THE α,α'-DIMETHYLADIPIC ACIDS, AND SEPARATION OF THE RACEMIC ACID INTO OPTICAL ISOMERS.

BY WILLIAM A. NOYES AND L. P. KYRIAKIDES.

Received June 24, 1910.

The α-α'-dialkyl-dicarboxylic acids are described in the literature as existing in two stereomeric forms—known as maleinoid and fumaroid. As far as we know none of these acids have been resolved into optical isomers. Bischoff and Walden[1] have failed in the resolution of the suc-

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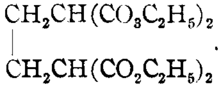
[1] *Ber.*, 22, 1814.

cinic acids. And because of this failure, the view has been entertained, that in such cases even saturated molecules are fixed in space, so that the singly-bound group or atom can not rotate.[1]

By glancing at the structure of α,α'-dimethyladipic acid, we see that this acid, like tartaric acid, has two asymmetric carbon atoms, and consequently, according to van't Hoff's theory, it ought to be resoluble into optical isomers. As will be seen later, we have succeeded in effecting this resolution.

Ethyl Ester of Butanetetracarboxylic Acid,



$$\begin{array}{l} CH_2CH(CO_3C_2H_5)_2 \\ | \\ CH_2CH(CO_2C_2H_5)_2 \end{array}$$

.—At first we prepared this compound in toluene. The best yield was obtained by using an excess of sodium, about one and one-half times that required theoretically in the malonic ester condensation. The sodium was shaken to granules in boiling toluene. The mixture was cooled, and equivalent portions of ethylene bromide and malonic ester were added. After three hours' cooling, the mixture was heated on the steam bath for about 15 hours. In this way from the pure malonic ester as well as from the recovered malonic ester, about 27–30 per cent. of the theoretical yield of butanetetracarboxylate boiling between 230–250° at 40 mm. was obtained.

Meunier[2] has described the use of magnesium in the form of amalgam instead of sodium in the preparation of mono- and diethylmalonic ester. We have tried this method in the preparation of butanetetracarboxylate, and find it better, in this case, than the use of sodium.

Ten grams of clean magnesium ribbon were put in a 500 cc. round-bottomed Jena flask, 400 grams of mercury added, and the mixture heated and shaken until the amalgamation was complete. The flask was then provided with a protected reflux condenser, 100 cc. of absolute alcohol was added, and the mixture heated on the steam bath for three hours. Occasional shaking of the flask, vigorously, hastens the formation of the magnesium ethylate by breaking the crust that clings to the sides of the flask. The flask was then cooled somewhat, and 100 grams of malonic ester were added, care being taken that the liquid did not boil too vigorously. When the reaction subsided, the flask was heated on the steam bath for three hours more. The alcoholic solution of the magnesium malonate was then cooled somewhat, 58 grams of ethylene bromide added, and after a short time the mixture was heated on the steam bath for 10–14 hours.

The alcohol was distilled off as much as possible under reduced pressure and the reaction mixture was treated with water and hydrochloric acid

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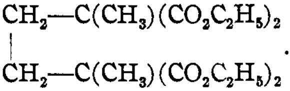
[1] Lean, *J. Chem. Soc.*, 65, 1001.

[2] *Compt. rend.*, 137, 714.

until the liquid separated into two layers. Ether was then added, the mixture shaken, and the ethereal solution separated and washed twice with dilute hydrochloric acid in order to wash away any magnesium held by the butanetetracarboxylate. After drying with sodium sulphate the ether was evaporated off, and the residue fractionated under reduced pressure. In this way 40–43 grams of the butanetetracarboxylate were obtained, boiling between 210–230° at about 10 mm. A low pressure is essential for successful fractionation of the product.

From each condensation about 40 grams of malonic ester were recovered, and used in subsequent condensations. The yield is, therefore, from 65 to 70 per cent. of the weight of malonic ester used or from 60 to 65 per cent. of the theoretical. The method is much less troublesome and, so far as we can judge from his statements, gives better yields than the method of Perkin.[1]

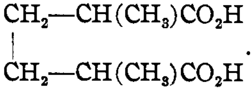
Ethyl Ester of Dimethylbutanetetracarboxylic Acid,



$$\begin{array}{l} CH_2\text{—}C(CH_3)(CO_2C_2H_5)_2 \\ | \\ CH_2\text{—}C(CH_3)(CO_2C_2H_5)_2 \end{array}$$

.—Ten grams of sodium were dissolved in about 120 cc. of absolute alcohol, the solution was cooled in ice water, and a mixture of 70 grams butanetetracarboxylate and 64 grams of methyliodide was added drop by drop, while the flask was continually shaken to keep the mixture from getting warm. It was found that the yield in the product was much greater when the mixture was kept thoroughly cooled. After the mixture had stood in the cold about half an hour it was warmed on the steam for an hour or two, while the flask was connected with an upright condenser. The alcohol was then evaporated off under reduced pressure. Water and a little hydrochloric acid were added. The ester was taken up in ether, washed with dilute potassium hydroxide, dried, the ether evaporated off, and the ester left to crystallize. The ester was purified by recrystallization from petroleum ether.[2] The yield of the recrystallized product was about 85 per cent. By working with smaller amounts we have succeeded in obtaining as high as 95 per cent. of the theoretical.

α-α'-Dimethyladipic Acids,



$$\begin{array}{l} CH_2\text{—}CH(CH_3)CO_2H \\ | \\ CH_2\text{—}CH(CH_3)CO_2H \end{array}$$

.—These were prepared from the pure crystallized dimethyl butanetetracarboxylate by the method of Lean[3] by boiling for 16 hours with a mixture of 350 cc. each of water and concentrated sulphuric acid. 165 grams of the dimethyl butanetetracarboxylate gave the theoretical amount of the adipic acids. The separation of the mixture into the two modifications, known

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[1] *J. Chem. Soc.*, 65, 578.

[2] Lean, *J. Chem. Soc.*, 65, 1004.

[3] *Loc. cit.*

as the fumaroid, and maleinoid, was carried out by a combination of the methods of Zelinsky[1] and Lean,[2] that is, by crystallizing from water and benzene. The final crystallizations were from water.

The dried acids melted at 143 and 70°. The lower melting modification begins to soften at 65°. Zelinsky gives the melting points as 140–141° and 74–76°. Lean gives 142° and 70–72°.

Separation of the Racemic α,α'-Dimethyladipic Acid into its Optical Isomers.—Twenty-seven grams of the acid melting at 70° were dissolved in 450 cc. of water, and 32 grams of brucine were gradually added to the hot solution. . 131 grams brucine are necessary to neutralize completely the 27 grams of the acid. We have used about one-fourth of the weight of brucine, theoretically required, with the object of forming the acid-salt of the less soluble optically active acid. The solution, while hot, was inoculated with a few crystals of the brucine salt from a former preparation, and the liquid left overnight. The crystals were collected on a filter, and washed four times with about 15 cc. of water each. They were then dissolved in 250 cc. of hot water and crystallized. One more crystallization from 150 cc. of water is all that is necessary.

The salt was dissolved in about 150 cc. water, decomposed with sodium hydroxide, cooled in ice, the solution of the sodium salt of the acid filtered off from the alkaloid, and the latter washed several times with cold water.

The aqueous solution was treated with hydrochloric acid, a little in excess of the amount required to neutralize the sodium hydroxide used. The acid was then extracted 5 times with ether, the latter evaporated off, and the acid crystallized once from a little water. The acid thus obtained gives a positive rotation of $(\alpha)_D^{28°} = +31.3°$ in 10 per cent. alcoholic solution. It begins to soften at 103.5° and melts completely at 105.5°. Yield, 7 grams A sample of the acid (0.1741 gram) titrated required 20.02 cc. 0.1 *N* potassium hydroxide. Theory, 20.00 cc. For the *l*-acid the mother liquor from the first crop of the brucine salt, in the preparation of the *d*-acid, was extracted with ether. The acid thus obtained melted at 70–95°.

Ten grams of this acid were dissolved in 150 cc. water and 11 grams of brucine added. The crystals that separated were recrystallized from diminishing amounts of water four times. The acid that was liberated and purified as in the case of the dextro acid, melted at 85–103° and gave a rotation of $(\alpha)_D^{28°} = -23.4$ in 10 per cent. alcoholic solution. A sample titrated required 4.02 cc. 0.5 *N* potassium hydroxide. Theory, 4.00 cc. The rotation in comparison with that of the dextro acid indicates that this acid still retained about 12 per cent. of the dextro form.

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[1] *Ber.*, 24, 3997.

[2] *J. Chem. Soc.*, 65, 1006.

Lack of time and material prevented us from carrying the purification of the levo form further.

An attempt to separate the fumaroid form of the α-α′-dimethyladipic acid (m. 143°) into optical isomers by means of its brucine salt was unsuccessful. It is undoubtedly a "meso" form, optically inactive by internal compensation.

Summary.

By using magnesium amalgam for the preparation of magnesium ethylate and condensing ethylene bromide with malonic ester by means of the latter the yield of butanetetracarboxylic ester has been greatly improved and this compound is now rather easily accessible.

The *dl*,α,α′-dimethyladipic acid (m. 70°) has been resolved into its optical components, of which the dextro form has been obtained in a state of purity. It melts at 104–105° and has a rotation $(\alpha)_D^{28°} = +31.3°$ in a 10 per cent. alcoholic solution.

The levo form was only obtained in a relatively impure form, melting over a wide range and given a rotation $(\alpha)_D = —23.4°$.

The "meso" form of α,α′-dimethyladipic acid (m. 143°) gave no indication that it could be separated into optically active components by crystallization with brucine.

The separation of the racemic α-α′-dimethyladipic acid into its optically active components definitely disproves the view expressed by Lean[1] that the carbon atoms are so united in this and similar cases that optical isomerism is impossible. These acids exist in four forms in close analogy with the four tartaric acids and in strict accord with the theory. The synthesis of laurolene from α-α′-dimethyladipic acid will be described in a subsequent paper.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. III. OXIDATION PRODUCTS OF *l*- AND *d*-LAUROLENE.[2]

BY WILLIAM A. NOYES AND C. G. DERICK.

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Levo-laurolene.

In a previous paper[3] it was shown that laurolene, when prepared from the nitroso derivative of aminolauronic anhydride by boiling with sodium hydroxide solution, always gave an optically negative hydrocarbon,

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[1] *Loc. cit.*

[2] Abstract of one part of a thesis presented by Mr. Derick to the Graduate School of the University of Illinois in partial fulfilment of the requirement for the degree of Doctor of Philosophy.

[3] Noyes and Derick, THIS JOURNAL, 31, 670.