

It was soluble in concentrated nitric and in concentrated sulfuric acid with a green-yellow fluorescence. An analysis gave the following results: Calcd. for  $C_{20}H_{12}O_3$ : C, 80.00; H, 4.00. Found: C, 79.87; H, 4.22.

Recrystallized from alcohol, it yields long bright prisms, which after giving off their alcohol of crystallization melt at  $180^\circ$ . The crystals gave the following analysis. Calcd. for  $C_{20}H_{12}O_3 \cdot \frac{1}{2}C_2H_5OH$ : C, 78.32; H, 4.64. Found: C, 78.08; H, 4.86. The substance is evidently fluorane.

Two grams of anhydrous copper phthalate was distilled very carefully. The fluorane obtained weighed 1.092 g., a yield of 91.5% of the theoretical.

The temperature of distillation must be above  $300^\circ$ . The quality of the distillate is only slightly influenced by the temperature, but much larger yields are obtained by strong heating.

Copper tetrachlorophthalate yields a similar distillate, but thus far the product has presented difficulties in the combustion for carbon and hydrogen and in the determination of chlorine. Presumably the product is dodecachlorofluorane, but checking analyses for carbon have not yet been obtained, since during the combustion small quantities of the compound distil through the red-hot copper oxide unburned and condense as minute crystals in the cold part of the tube. The combustion, while giving a low value for carbon, gives only a very small fraction of a per cent. of hydrogen, this latter corresponding to a dodecachlorofluorane, which would contain no hydrogen. The Carius method for chlorine yields varying low values for chlorine, around 58%, while the calculated value is 59.49%. Other methods for chlorine also yield low results.

### Summary

Dry distillation of anhydrous copper phthalate at high temperatures (between  $300^\circ$  and dull red heat) gives fluorane, which may be obtained in as high a yield as 91.5%.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF GRINNELL COLLEGE]

## DECOMPOSITION OF OPTICALLY ACTIVE DIAZO COMPOUNDS<sup>1</sup>

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RECEIVED APRIL 24, 1930

PUBLISHED JULY 3, 1930

The aliphatic diazo group may be formulated as a straight chain or as a ring.



The chain structure was established largely by the work of Angeli,<sup>2</sup> Thiele,<sup>3</sup> and Staudinger,<sup>4</sup> who obtained chain derivatives of diazo compounds.

alcohol had been driven off, a portion of the alcohol-free substance was *melted*, whereas the melting point of fluorane is  $180^\circ$ .

<sup>1</sup> Presented before the 79th meeting of the American Chemical Society, Atlanta, Georgia, April 10, 1930.

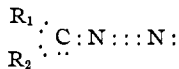
<sup>2</sup> A. Angeli, *Atti accad. Lincei*, [V] 32, i, 443 (1923).

<sup>3</sup> J. Thiele, *Ber.*, 44, 2522 (1911).

<sup>4</sup> Staudinger, *Helv. Chim. Acta*, 5, 75 (1922).

Recently there has been a disposition to revert to the ring structure. Lindemann and Thiele<sup>5</sup> as a result of studies of the parachors assign a ring structure to the azides, and Sidgwick<sup>6</sup> from a comparative study of boiling points is now inclined to favor the ring structure for both azides and diazo compounds. On the other hand, Mumford and Phillips<sup>7</sup> conclude that the parachor does not enable them to decide between the ring and chain formulas for the diazo group. Forster and Newman<sup>8</sup> had previously reached a similar conclusion.

If we assume a straight chain structure, then one of the carbon-nitrogen bonds is a polar valence and the other is a co-valence and together they form what is termed a semipolar double bond. The adjacent nitrogen loses one electron to the carbon and the asymmetry of the carbon atom results from a localization of this charge much the same as the localization of the ordinary bond is considered to cause asymmetry.<sup>9</sup>



Quadrivalent sulfur compounds of the type  $\begin{array}{c} R_1 \\ \vdots \\ R_2 \end{array} \cdot \overset{+}{S} : \ddot{O} :$  have been pre-

pared and resolved into optical isomers,<sup>10</sup> showing that the positive charge is localized on the sulfur atom. The existence of a polar valence in quadrivalent sulfur was demonstrated by Sugden.<sup>11</sup>

In 1921 Levene and Mikeska<sup>12</sup> and in 1922 Noyes and Chiles<sup>13</sup> prepared optically active esters in which the only possible asymmetric carbon was that doubly bound to diazo nitrogen. This work has been criticized because the rotations of the compounds investigated were so small that impurities might have caused the observed rotation.

In 1926 Kendall and Noyes<sup>14</sup> obtained optically active diazo derivatives from both camphoric acid and *l*-isocamphoric acid. Camphoric acid and its derivatives, however, contain two asymmetric carbon atoms, but when strain is introduced into the molecule the secondary carbon only is racemized and the *l*-iso- compound is formed. Though Kendall prepared optically active diazo derivatives from both types of compounds, their instability precluded any decision as to the activity of the secondary carbon which was attached to the diazo group.

<sup>5</sup> Lindemann and Thiele, *Ber.*, **61**, 1529 (1928).

<sup>6</sup> Sidgwick, *J. Chem. Soc.*, 1108 (1929).

<sup>7</sup> Mumford and Phillips, *ibid.*, 2112 (1929).

<sup>8</sup> Forster and Newman, *ibid.*, **97**, 2572 (1910).

<sup>9</sup> W. A. Noyes, *Chem. Rev.*, **5**, 549 (1928).

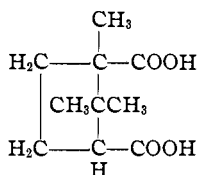
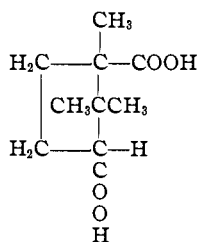
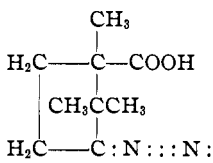
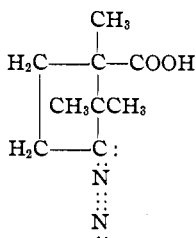
<sup>10</sup> Phillips, *J. Chem. Soc.*, **127**, 1525 (1925); 2079 (1926); 188 (1927).

<sup>11</sup> Sugden, *ibid.*, **125**, 1177 (1924); **127**, 1528 (1925); 1173 (1927).

<sup>12</sup> Levene and Mikeska, *J. Biol. Chem.*, **45**, 592 (1911); **52**, 485 (1922).

<sup>13</sup> Chiles with Noyes, *THIS JOURNAL*, **44**, 1798 (1922).

<sup>14</sup> Kendall with Noyes, *ibid.*, **48**, 2404 (1926).

Camphoric acid (*cis*)*l*-Isocamphoric acid (*trans*)*cis*-dialzo*trans*-dialzo

Skinner<sup>15</sup> has studied quite thoroughly the decomposition of aminolauronic ester, derived from the *cis* acid by substitution of the amino group for the secondary carboxyl; and Skinner and Noyes<sup>16</sup> have studied the decomposition of the *trans*-amino ester, similarly derived from the *l*-isocamphoric acid. They found for the decomposition of the *cis*-amino ester, 40 parts of hydroxy to 60 parts of unsaturated esters, and for the *trans*-amino ester, 60 parts of hydroxy to 40 parts of unsaturated esters. An ether acid was found only in the decomposition of the *trans* compound. There is, however, no direct proof that in these decompositions diazo compounds are formed as intermediates.

In this work we undertook to prepare the actual diazo compounds, to decompose them under identical conditions, and to study their decomposition products. By this method we have obtained definite evidence that the two compounds differ. From the decomposition of 20 g. of the *cis*-dialzo compound we found 60.5% of unsaturated ester. This corresponds to the amount found by Skinner for the *cis*-amino compound. No ether acid was found.

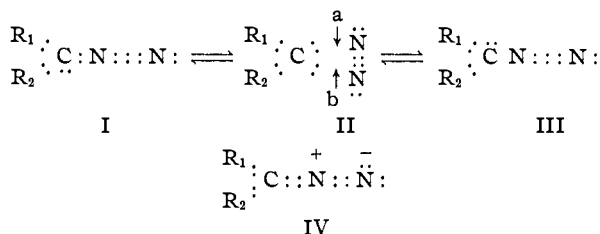
In the decomposition products of the *trans*-dialzo derivative we isolated the ether acid that Skinner found only in the decomposition of the *trans*-amino ester. Unsaturated esters were present to the extent of 27%.

A consideration of the conflicting physical evidence, together with the fact that the products of decomposition are partly the same, furnishes justification for the view that the chain and ring formulas represent tauto-

<sup>15</sup> Skinner, *THIS JOURNAL*, **45**, 1498 (1923).

<sup>16</sup> Skinner and Noyes, *ibid.*, **39**, 2692 (1917).

meric modifications that exist in equilibrium. This would account for the ease with which the active form racemizes.



The transition from the ring to the chain form may occur by a fission in the ring at either point (a) or at point (b). When the carbon-nitrogen bond breaks, the carbon must retain both electrons, for if both electrons went with the separating nitrogen, this nitrogen would be negative, the nitrogen adjacent to the carbon positive, and the compound optically inactive (form IV). If one of the electrons forming this severed carbon-nitrogen bond went with the carbon and the other with the nitrogen, neither the carbon nor the remote nitrogen would have a complete octet.


If the ring II opens at (a) then form III will result, while if fission occurs at (b), form I will be obtained. The carbon retaining the electrons being negative and the remote nitrogen positive, the free electrons on the nitrogen adjacent to the carbon will shift and occupy a place between the two nitrogen atoms. All atoms have completed octets in this interpretation.<sup>17</sup>

That we obtained different products on decomposition of the *d*- and *l*-forms was undoubtedly due to the slowness with which the active forms approach equilibrium at the low temperatures employed.

### Experimental Part

*d*-Camphoric acid was prepared by the oxidation of *d*-camphor with nitric acid. A total of fifty pounds of camphor was used in this work. The camphoric acid was converted into the anhydride by boiling with acetic anhydride. On heating with ammonium hydroxide under pressure by the method of Noyes and Taveau,<sup>18</sup> a mixture of the ammonium salts of  $\alpha$ - and  $\beta$ -*d*-camphoramidic acids resulted which was separated by the difference in solubility of their ammonium and sodium salts.

Aminocamphonic acid was obtained from the  $\alpha$ -*d*-camphoramidic acid by means of the hypobromite reaction.

The anhydride of aminocamphonic acid,  $C_8H_{14}$   was prepared by the method of Noyes and Potter<sup>19</sup> by heating aminocamphonic acid with acetic anhydride and sodium acetate. It was also prepared by distilling the amino acid with chalk.

<sup>17</sup> Lindemann, Wolter and Groger, *Ber.*, **63**, 702 (1930), from a study of the parachors, refractive indices and absorption spectra also reach the conclusion that the diazo group is mostly cyclic but partly open chain that may exist in an optically active form.

<sup>18</sup> Noyes and Taveau, *Am. Chem. J.*, **32**, 287 (1904).

<sup>19</sup> Noyes and Potter, *THIS JOURNAL*, **37**, 189 (1915).

The nitroso anhydride precipitated on passing nitrogen trioxide into the ice-cold aqueous solution of the amino anhydride. It was recrystallized from alcohol, giving light yellow needles, m. p. 138–139°; 60 g. of the pure compound was obtained. The rotation of 2.5 g. in 100 cc. of absolute alcohol was  $[\alpha]_D^{24}$  157.6°. Noyes and Potter give  $[\alpha]_D^{24}$  153°.

The *cis*-dialo derivative was prepared from the nitroso anhydride by the method of Kendall and Noyes,<sup>20</sup> which consists of treating the ethereal solution of the nitroso anhydride at 20° with sodium methylate. Light red crystals were obtained which melted, when pure, at 30–32° when placed in a bath at 25° and heated rapidly.

Twenty-one and two-tenths grams of the crystalline compound was obtained. On decomposition in ether solution with dilute sulfuric acid, 16.24 g. of material resulted. The ether solution was washed with dilute sodium carbonate solution to extract any ether acid but none was found.

From the 16.24 g. of material there was obtained by two refractionations 9.83 g. of unsaturated ester which boiled at 56° (3 mm.). The remainder boiled between 70 and 100°. A residue of 2.0 g. was left in the flask. The unsaturated ester, therefore, makes up 60.53% of the decomposition products (compare Skinner).

### The *trans*-Derivatives

*l*-Isocamphoric acid was prepared by the method of Noyes and Knight,<sup>21</sup> in which *d*-camphoric acid is heated in sealed tubes with acetic and hydrochloric acids. A total of 1570 g. was obtained. This was converted into  $\alpha,\beta$ -dimethyl *l*-isocamphorate which had the following constants:  $[\alpha]_D^{25}$  –67.7°;  $d_4^{25}$  1.0746; b. p. 117–118° (4 mm.). Noyes and Skinner give  $[\alpha]_D^{24,5}$  –65.5°. This dimethyl ester was hydrolyzed to the  $\beta$ -methyl *l*-isocamphorate, which was converted to the  $\beta$ -methyl  $\alpha$ -*trans*-camphoramidate using the method of Noyes and Skinner.

**Methyl *trans*-Amino-camphonate.**—Considerable difficulty was experienced in preparing this ester in good yield; 60 g. of the  $\beta$ -methyl  $\alpha$ -*trans*-camphoramidate cooled to –20° was treated with 60 g. of bromine dissolved in a well-cooled 10% solution of sodium hydroxide. After standing for one hour, during which it had warmed up to 0°, it was heated for twenty to thirty minutes on the steam-bath. The oily layer which separated was extracted, dried, and distilled; yield, 30 g.; b. p. 112° (5–6 mm.).

**Mono-urea from Methyl *trans*-Aminocamphonate.**—This compound was prepared by mixing 30 g. of methyl-*trans*-aminocamphonate with a solution of 20 g. of nitrourea in 100 cc. of water.<sup>22</sup> On standing the mono-urea crystallized out and was recrystallized from alcohol; m. p. 155°.

**Di-urea from Methyl *trans*-Aminocamphonate.**—The mono-urea was treated in ether solution with nitrogen trioxide forming the isocyanate. On adding an equivalent of methyl *trans*-aminocamphonate crystals of the di-urea often separated. Sometimes an oil precipitated which was dissolved by adding more ether. Then on slowly adding 10% sodium hydroxide the di-urea precipitated in about 75% yield; m. p. 305°. This is the melting point obtained by Kendall and Noyes.

*Anal.* (Kjeldahl). Subs., 0.1521 required 7.78 cc. of *N*/10 HCl. Calcd. for  $C_{21}H_{36}O_6N_2$ ; N, 7.06. Found: 7.16.

**Nitroso Derivative of Di-urea.**—The di-urea was suspended in absolute ether at –20° and dry nitrogen trioxide was passed in for four to five hours. After standing overnight the ether solution was washed with ice water. Air was blown through the

<sup>20</sup> Kendall with Noyes, *THIS JOURNAL*, **48**, 2404 (1926).

<sup>21</sup> Noyes and Knight, *ibid.*, **32**, 1670 (1910).

<sup>22</sup> Compare Davis and Blanchard, *ibid.*, **51**, 1790 (1929).

mixture for about an hour, during which time the water was frequently changed. As the ether evaporated, crystals of the nitroso derivatives were deposited on the sides of the flask. On recrystallization from ether sulfur-colored, microscopic, rectangular plates melting at  $78^{\circ}$  were obtained. This compound is very unstable and tends to revert to the di-urea even when kept in a desiccator over calcium chloride. A Kjeldahl analysis gave results corresponding to the di-urea.

**trans-Diazo Derivative.**—The nitroso compound was dissolved in absolute ether and treated with one equivalent of sodium in absolute methyl alcohol. A deep red solution resulted. This was washed several times with water to remove the sodium hydroxide and the residual half of the urea molecule. The ether solution was then dried by freezing to  $-80^{\circ}$  with a mixture of solid carbon dioxide and acetone. The clear ether solution was siphoned off and on evaporation the solid diazo resulted. It was not possible to purify this material by recrystallization, as the compound showed a tendency to decompose when warmed to about  $-15^{\circ}$  and such attempts only resulted in making the material less pure. The purity of the diazo compound varied in the several runs from 89 to 92%. The diazo compound was decomposed by acidifying at  $-20^{\circ}$  with dilute sulfuric acid. The ethereal solution was washed with sodium carbonate to extract the ether acid. The ethereal layer was dried, the ether distilled and the residue twice fractionated under reduced pressure; 32.12 g. of decomposition products gave 8.66 g. of unsaturated ester boiling at  $90-95^{\circ}$  (32 mm.). The remainder boiled at a temperature above  $110^{\circ}$ . The unsaturated fractions make up 26.96% of the total.

**Methyl Ether of *cis*-Camphonolic Acid.**—The sodium carbonate extract was warmed with bone black, filtered, acidified and extracted with ether. The crystals from ether were recrystallized twice from alcohol and melted at  $86-87^{\circ}$ .

*Anal.* Subs., 0.0675: Ag, 0.0245. Calcd. for  $\text{AgC}_{10}\text{H}_{17}\text{O}_3$ : Ag, 36.86. Found: Ag, 36.30.

Since this paper was submitted for publication, additional evidence has been obtained showing that the *cis* and *trans* diazo compounds differ. Kendall<sup>14</sup> showed that the *cis* diazo compound spontaneously decomposed to give the bis-hydrazone of Noyes and Taveau,<sup>13</sup> m. p.  $97^{\circ}$ . When, however, the *trans* diazo compound was allowed to decompose in the same manner, a compound of high molecular weight (320-340) was obtained which melted at  $71^{\circ}$ . A mixed melting point gave  $59-62^{\circ}$ . These compounds may also be *cis-trans* isomers.

The writer expresses his thanks to the directors of the W. S. Hendrixson Memorial Fund of Grinnell College for a grant that defrayed part of the expenses of this investigation. Thanks are also due Miss Martha Hemphill and Mr. Ralph Bunting for the preparation of materials, to Dr. G. S. Skinner for gifts of camphoric acid and camphoric anhydride, and to Professor W. A. Noyes for his kindly interest and advice.

### Summary

From a study of the decomposition of diazo derivatives of the methyl esters of both *cis*-aminocamphonanate and *trans*-aminocamphonanate, evidence has been secured that a carbon atom attached to the diazo grouping retains its asymmetry.

The methyl ether of *cis*-camphonolic acid is found *only* in the decom-

position products of the *trans*-diazo compound. The proportion of the unsaturated ester is different in the two decompositions.

The two diazo compounds give by their decomposition approximately the following products: *cis*-diazocamphonanic methyl ester

Esters of hydroxy acids.....	39.5%
Esters of unsaturated acids.....	60.5%

*trans*-diazocamphonanic methyl ester

Methyl ether of <i>cis</i> -camphonolic acid.....	5.0%
Esters of hydroxy acids.....	68.0%
Esters of unsaturated acids.....	27.0%

The above results furnish conclusive proof that the two diazo compounds have an asymmetric structure, in part. This is most simply explained by the electronic formulas



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[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

### NORMAL VALEROLACTONE. III. ITS PREPARATION BY THE CATALYTIC REDUCTION OF LEVULINIC ACID WITH HYDROGEN IN THE PRESENCE OF PLATINUM OXIDE

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RECEIVED APRIL 25, 1930

PUBLISHED JULY 3, 1930

*n*-Valerolactone has been prepared in the past by reducing levulinic acid to  $\gamma$ -hydroxyvaleric acid and then removing the elements of a molecule of water from the latter. Reduction of the levulinic acid has been effected either through the agency of sodium amalgam<sup>1</sup> or of ethyl alcohol and sodium,<sup>2</sup> procedures which are time-consuming, expensive and ill-suited to the preparation of this lactone in quantity.

The basis for a simplification and an improvement in method of preparation was announced some years ago by Sabatier and Mailhe,<sup>3</sup> who by passing levulinic acid in gas phase together with hydrogen over a nickel catalyst at 250° succeeded in hydrogenating the former and dehydrating the resulting reaction product all in one operation. Certain facts<sup>4</sup> recently ascertained with respect to the stability of *n*-valerolactone at its boiling point having cast some doubt upon the quality of a product obtained at

<sup>1</sup> Wolff, *Ann.*, **208**, 104 (1881).

<sup>2</sup> Losanitsch, *Monatsh.*, **35**, 301 (1914); Schuette and Sah, *THIS JOURNAL*, **48**, 3163 (1926).

<sup>3</sup> Sabatier and Mailhe, *Ann. chim. phys.*, [8] **16**, 78 (1909).

<sup>4</sup> Schuette and Thomas, *THIS JOURNAL*, **52**, 2028 (1930).