

very satisfactory as shown by the vertical lines under the peaks in the figure.

The other intensity curves are quite unsatisfactory. Curve B is of some interest because it lacks the fine structure on the inside of the first minimum which appears on the other curves, apparently as a result of the terms above 4 Å. The possibility of obtaining a satisfactory curve with any reasonable variation of Model A seems remote. One cause of the disagreement with Curve A is revealed by the width and position (1.42 Å.) of the first peak of the radial distribution function. For Model A one would expect instead a rather sharp peak at about 1.34 Å. with weak shoulders or satellites at 1.46 Å. and 1.09 Å. Another factor is the absence of any distance which would correspond to the radial distribution peak at 4.12 Å.

Our electron diffraction investigation thus leads to the conclusion that perylene is 1-methyl-2-

vinylacetylene (Structure II) with the bond distances and bond angles which were assumed for Model E from the existing information regarding similar molecules. Because the agreement of the photographs and the radial distribution function with Model E is so detailed that it could hardly be fortuitous, we should have confidence in this conclusion even if no effort to eliminate other possible formulas had been made.

### Summary

The electron diffraction investigation of perylene shows it to be 1-methyl-2-vinylacetylene. The structural parameters found were those anticipated from a knowledge of the structures of similar molecules.

An approximation to the radial distribution integral which is more accurate than the usual summation is briefly described.

PASADENA, CALIFORNIA

RECEIVED JULY 7, 1942

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 894]

## Cyclobutane Derivatives. I.<sup>1</sup> The Degradation of *cis*- and *trans*-1,2-Cyclobutanedicarboxylic Acids to the Corresponding Diamines

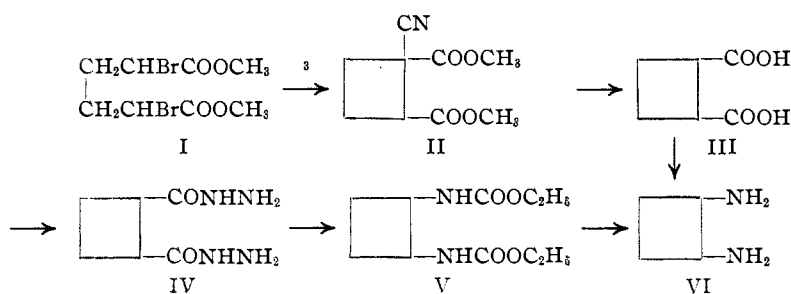
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According to scattered references in the literature,<sup>2</sup> the Curtius degradation of cyclic dicarboxylic acids proceeds in the normal fashion without change in configuration. In the present work it was found that the *cis*- and *trans*-isomers (III) could be converted, over the intermediates (IV) and (V), into the corresponding diaminocyclobutanes (VI). The diamine obtained from the *cis*-acid was shown to possess the *cis*-structure by the preparation from it of cyclic derivatives; under the same conditions cyclic products were not obtained from *trans*-(VI).

(1) The results contained in this and the two following papers were presented before the Pacific Division of the American Association for the Advancement of Science at the Pasadena Meeting, June, 1941.

(2) (a) Curtius, *J. prakt. Chem.*, [2] **91**, 23 (1915); (b) Diels, Blom and Koll, *Ann.*, **443**, 242 (1925); (c) Alder and Stein, *ibid.*, **514**, 211 (1934). However, in the case of the 1,3-cyclohexanedicarboxylic acids, Skita and Rössler [*Ber.*, **72**, 461 (1939)] claim that the same diurethan results both from the *cis*- and from the *trans*-diazide.

The K. F. Schmidt degradation<sup>4</sup> had not previously been applied to cyclic dicarboxylic acids. When *cis*- and *trans*-(III) were treated with



hydrazoic acid according to this method they were transformed directly, with retention of configuration, to *cis*- and *trans*-(VI); thus the method affords an alternative preparative route to these substances.

(3) Fuson and Kao, *THIS JOURNAL*, **51**, 1536 (1929); Ellingboe and Fuson, *ibid.*, **56**, 1774 (1934).

(4) Hurd in Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 698. From succinic acid a small yield of ethylenediamine has been obtained (Oesterlin, *Angew. Chem.*, **45**, 536 (1932)).

### Experimental<sup>5</sup>

The cyclobutanedicarboxylic acids (III) were made by the method<sup>3</sup> of Fuson employing both the methyl and the ethyl esters of the intermediates. The use of the methyl esters is to be recommended as pure crystalline meso (I) can more conveniently be prepared than the corresponding diethyl ester. It is possible to utilize the crude liquid racemic dibromoadipic esters for ring closure or for conversion to the crystalline isomers but, since the crude esters contain<sup>6</sup> some  $\alpha,\alpha$ -dibromo isomer, additional purification steps are necessary.

**$\alpha,\alpha'$ -Dibromoadipic Dimethyl Ester (I).**<sup>7</sup>—Adipic acid (1460 g. = 10 moles) was treated in all glass apparatus with thionyl chloride<sup>7b,8</sup> (2380 g. = 3% excess); the latter was added at two to three hour intervals in portions of about 750 g. while heating at 70–80°. When reaction was complete, 3520 g. of bromine (10% excess) was added dropwise (eighteen hours) with continued heating and the product finally heated for eight hours at 100°. The crude acid halide was added with stirring to 2000 cc. of methyl alcohol in a flask surrounded by an ice-bath; meso (I) crystallized on seeding and cooling. After filtering and washing with methanol the yield was about 50%. Crude (I) was recovered from the filtrate by distillation,<sup>7b</sup> b. p. ca. 163° at 3 mm., average<sup>9</sup> total yield 93%. Additional meso (I) was obtained from the distillate, needles, m. p. 73.5–74.0° from methanol, average total yield 2329 g. = 70% (corresponding yield in case of the diethyl ester, 46%).

The non-crystalline distillate consisted largely of the unstable racemic modification, which crystallized out slowly at about –10°. It was obtained pure by recrystallization from methanol at –78°, m. p. +11–12°.

*Anal.* Calcd. for  $C_8H_{12}Br_2O_4$ : C, 28.94; H, 3.64. Found: C, 29.07; H, 3.86.

**1-Cyano-1,2-cyclobutanedicarboxylic Acid Dimethyl Ester (II).**—Two moles<sup>10</sup> of meso<sup>11</sup> (I) (664 g.), 368 g. (5.5 moles) of potassium cyanide (Merck reagent<sup>12</sup>) and 360 cc. of methanol were refluxed for fifty-six hours from an oil-bath maintained at about 75°; occasional stirring was necessary to break up the solid cake which formed. The product was taken up in anhydrous ether and fractionated *in vacuo*; the average yield, b. p. ca. 128° at 3 mm. was 284 g. = 72% (82% in the ethyl ester series). The distillate crystallized in part; the resulting crystals (26% of the weight of the distillate) were recrystallized from methanol, colorless needles m. p. 89.5–90.0°. The

(5) All melting points are corrected. The authors are indebted to Dr. G. Oppenheimer and Mr. G. A. Swinehart for microanalyses reported in this and the two following papers.

(6) Ingold, *J. Chem. Soc.*, **119**, 956 (1921).

(7) (a) Le Sueur, *ibid.*, **95**, 275 (1909); (b) Stephen and Weizmann, *ibid.*, **103**, 271 (1913); (c) Bernton, Ing and Perkin, *ibid.*, **125**, 1492 (1924).

(8) Fuson, Kreimeier and Nimmo, *THIS JOURNAL*, **52**, 4074 (1930).

(9) Average yields reported in this paper are based on the results of six or more identical experiments.

(10) A ten-mole batch gave only a 40% yield due to decomposition during distillation of the crude product.

(11) The racemic form of (I) behaved in the same way, giving a comparable yield of crystalline and liquid (II) with the latter predominating.

(12) A commercial grade of sodium cyanide proved satisfactory for effecting ring closure of the meso diethyl ester in ethanol but its use in the present instance led to extensive tar formation.

non-crystalline part<sup>13</sup> was refractionated and the portion boiling at 119–120° at 2 mm. subjected to analysis; this material did not crystallize at 0°.

*Anal.* Calcd. for  $C_9H_{11}NO_4$ : C, 54.82; H, 5.62; N, 7.10. Found (solid): C, 55.15; H, 5.62; N, 7.15. Found (liquid): C, 54.49; H, 5.62; N, 6.85.

**1,1,2-Cyclobutanetricarboxylic Acid.**—This acid was prepared from crystalline (II) following essentially the procedure of Fuson.<sup>3</sup> The colorless barium salt was decomposed with the requisite amount of sulfuric acid and the filtrate evaporated *in vacuo*. The crystalline residue consisted of hydrated tricarboxylic acid, m. p. 135° dec. from dioxane on addition of benzene. The water of crystallization was not lost on drying *in vacuo* under the usual conditions; in one experiment which we have not since been able to reproduce, water was apparently removed during recrystallization. The anhydrous acid, colorless massive prisms from anhydrous ether in which it is soluble without difficulty at room temperature, melted at 91–92° and began to lose carbon dioxide at about 130°.

*Anal.* Calcd. for  $C_7H_8O_6$ : C, 44.69; H, 4.29. Found: C, 44.90; H, 5.12.

On treatment with water, the acid was reconverted to the stable hydrate.

**cis- and trans-1,2-Cyclobutanedicarboxylic Acids (III).**—The crude liquid isomer (II) (789 g.) was refluxed with 2000 cc. of 6 *N* hydrochloric acid for twenty-four hours, the hydrolyzate evaporated on the steam-bath and the residue extracted with anhydrous ether (acetone may also be used). After removal of solvent, the crude acid was decarboxylated by heating at 170–180° at 20 mm. for three hours and the mixture refluxed<sup>14</sup> for an additional three hours with 2000 g. of acetyl chloride. Acetyl chloride and acetic acid were distilled off; the material remaining was heated from an oil-bath at 150–160° at 20 mm. for several hours and finally distilled at 2 mm. An 81% yield of *cis*-anhydride was obtained boiling at 127–130°; a portion was recrystallized from benzene, blades, m. p. 76.5–77.0°. Distillation residues from several runs were combined and subjected to a second treatment with acetyl chloride; a small additional amount of anhydride was recovered.

*cis*-Anhydride was heated to boiling with 0.8 its weight of water; *cis*-acid crystallized from the resulting solution on cooling. Saturation of the filtrate with dry hydrogen chloride yielded additional amounts of less pure material. The yield of *cis*-(III) was 85%; from benzene–dioxane it crystallized in rectangular prisms exhibiting extensive twinning, m. p. 139.5–140.0°. From the residual mother liquors, recovery was best effected via the anhydride.

*trans*-(III) has been prepared from the *cis*-isomer by treatment with hydrochloric acid<sup>15</sup>; in the present investi-

(13) A portion which had stood in a loosely stoppered bottle for a year had deposited a small amount of crystals, colorless rectangular prisms from methanol, m. p. 172.5–173.5° dec., easily soluble in water and hot methanol, difficultly soluble in ether. Analyses point to the formula  $C_{10}H_{12}N_2O_5$ : Calcd.: C, 50.00; H, 5.04; N, 11.66. Found: (average) C, 50.23; H, 5.43; N, 11.36. The substance may be related to  $\alpha,\alpha'$ -dicyanoadipic ester.

(14) *trans*-(III) is converted by this treatment to a mixed anhydride with acetic acid which on stronger heating decomposes into *cis*-anhydride; compare however reference 15.

(15) Perkin, *J. Chem. Soc.*, **65**, 572 (1894).

gation two further methods for effecting the isomerization were found. *trans*-(III) may also conveniently be prepared, although the method is expensive, from the readily obtainable *trans*-dihydrazide (IV) by hydrolyzing with boiling 6 *N* hydrochloric acid and isolating by continuous extraction with ether.

*cis*-(III) (50 g.), heated<sup>16</sup> under reflux from a bath at 200° for five hours was partially isomerized. Recrystallization of the product from water yielded 25.5 g. of *trans*-(III), clusters of blades from benzene-dioxane, m. p. 130.5–131.0°.

Twenty grams of *cis*-(III) dimethyl ester was heated under reflux from a water-bath for two and one-half hours with 0.3 g. of sodium dissolved in 5 cc. of methyl alcohol.<sup>17</sup> The product was washed with water, dried and distilled, giving 16.3 g. of ester, b. p. 118–119° at 24 mm. A portion of this ester, hydrolyzed by heating with dilute hydrochloric acid, yielded 76% of *trans*-(III). From another portion the *trans*-dihydrazide (IV) was obtained in 86% yield; the amount of *cis*-ester present in the equilibrium mixture<sup>18</sup> must, therefore, be small.

*cis*- and *trans*-(III) Esters.—Pure *cis*-(III) dimethyl ester was prepared in 94% yield from the acid with diazomethane, b. p. 85° at 3 mm. On a preparative scale the diethyl ester was made by heating under reflux 500 g. of *cis*-(III) (anhydride could be used directly) for four hours with 2000 cc. of absolute alcohol while passing in a slow stream of dry hydrogen chloride. The reaction mixture was then poured into water and worked up in the usual manner. The yield was 493 g. (71%), b. p. 99–100° at 2 mm., 123° at 24 mm.; this ester contained at most only small amounts of *trans*-isomer (best detected by the reaction with hydrazine hydrate). Incompletely esterified acid in the water and carbonate washings was recovered by evaporation and conversion to anhydride.

A suitable source material for the preparation of large amounts of *trans*-(IV) was made directly from crude (III), resulting from saponification of crude liquid (II) and subsequent decarboxylation. This was esterified by heating with alcohol, carbon tetrachloride<sup>19</sup> and aqueous hydrochloric acid; an average yield of 82% of a mixture consisting of about equal amounts of each isomer was obtained (in the case of the cyano diethyl ester intermediate, the average yield was 71% of a similar product).

*cis*- and *trans*-1,2-Cyclobutanedicarboxydihydrazides (IV).—These compounds were prepared by adding *cis*- and *trans*-(III) esters dropwise to 10% excess of hydrazine hydrate (85%) which was heated under reflux from an oil-bath at 130° (lower temperatures gave incomplete reaction) and continuing the heating at this temperature for five hours. Under these conditions a practically quantitative yield of crude (IV) resulted. No changes in configuration took place; *cis*- and *trans*-(IV) on acid hydrolysis gave, respectively, *cis*- and *trans*-(III).

From *cis*-(III) dimethyl ester an 80% yield of *cis*-(IV) was obtained. On a preparative scale, 246 g. of *cis*-(III) diethyl ester was treated with 160 g. of 85% hydrazine

hydrate. The product was allowed to crystallize in the ice-chest, was filtered off and washed with alcohol; the filtrates were evaporated and the residue pressed on tile. The combined crude material was refluxed for a short while with 500 cc. of absolute alcohol (not sufficient to effect complete solution); after cooling and filtering, 160 g. (75%) of substantially pure *cis*-(IV) was obtained. The mother liquors did not usually afford crystalline material and were hydrolyzed for recovery of (III). In a few cases the m. p. of the crude indicated an admixture of *trans*-isomer arising probably from impurity in the *cis*-(III) ester used; separation was effected by digesting the crude (IV) with an amount of 85–90% ethanol sufficient to dissolve the *cis*-isomer and filtering hot. The greater part of *cis*-(IV) could be recovered from the filtrate.

*cis*-(IV) crystallized from absolute alcohol in massive prisms which exhibit extensive twinning, m. p. 140.0–140.5°. Occasionally when recrystallized from this solvent a second metastable form was encountered which was separated mechanically, clusters of fine needles, m. p. 134.5–135.0°, mixed m. p. with the stable form 135–140°; on standing it is transformed to the stable variety. *cis*-(IV), over a period of months, was largely converted into material of different composition difficultly soluble in water and the common organic solvents.

It was found convenient to prepare the *trans*-isomer from *cis*-, *trans*-(III) diethyl ester mixtures (see above); *trans*-(IV) crystallized from the reaction mixture and *cis*-isomer could be isolated from the mother liquors (better to hydrolyze for recovery of (III)). *trans*-(IV) was purified by recrystallization from 50% aqueous alcohol, clusters of colorless needles, m. p. 223.0–223.5°. The (III) ester mixture from crude liquid (II) gave an average yield of 54% while the ester mixture from cyano diethyl ester gave a 48% yield.

*Anal.* Calcd. for C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>O<sub>2</sub>: C, 41.85; H, 7.02; N, 32.54. Found (*cis*-needles): C, 42.03; H, 6.92; N, 32.74. Found (*cis*-prisms): C, 41.71; H, 7.01; N, 32.70. Found (*trans*): C, 42.18; H, 7.01; N, 32.89.

*cis*- and *trans*-(IV) Dihydrochlorides.—To 100 g. of *cis*-(IV) suspended in an equal weight of water and surrounded by an ice-bath, 98 cc. of concentrated c. p. hydrochloric acid was added dropwise with stirring during twenty minutes. A further addition of 100 cc. excess of hydrochloric acid caused the precipitation of the dihydrochloride which was filtered off on a sintered glass filter, washed with cold absolute alcohol and dry ether and dried in a desiccator over sodium hydroxide, yield 78.5 g. (55%). The material is easily altered; it was analyzed without further purification. Additional amounts contaminated with hydrazine hydrochloride were obtained from the mother liquors by saturating with hydrogen chloride gas at 0°; such material could also be used for the preparation of *cis*-(V).

*trans*-(IV) (250 g.) was suspended in 300 cc. of water and the theoretical amount of concentrated hydrochloric acid (242 cc.) added during twenty minutes as above. Excess acid (500 cc.) was added and the precipitate isolated as before, yield 342.5 g. (96%). A portion was recrystallized by dissolving in methanol at 25° and cooling to 0°, compact rosetts of fine needles, m. p. about 200° dec.

(16) Compare Liebermann, *Ber.*, **22**, 2245 (1889); Stoermer and Bachér, *ibid.*, **55**, 1865 (1922); Skita and Rössler, *ibid.*, **72**, 271 (1939).

(17) Compare Hüchel and Goth, *ibid.*, **58**, 447 (1925).

(18) Compare ref. 2c.

(19) Hultman, Davis and Clarke, *This Journal*, **43**, 366 (1921).

*Anal.* Calcd. for  $C_6H_{14}Cl_2N_4O_2$ : C, 29.40; H, 5.76; N, 22.86. Found (*cis*): C, 29.67; H, 6.06; N, 23.19. Found (*trans*): C, 29.73; H, 6.02; N, 22.76.

*cis*- and *trans*-N,N'-Dicarbethoxy-1,2-diaminocyclobutanes (V).<sup>20</sup>—*cis*-(IV) dihydrochloride (100 g.) was dissolved in 100 cc. of water, the solution layered with 700 cc. of anhydrous ether and a solution of 56.2 g. of sodium nitrite in 120 cc. of water was added over a period of fifteen minutes with continuous stirring, maintaining the temperature at 13–16°<sup>21</sup> (cooling bath at –15°). Stirring with cooling was continued for an additional five minutes; the ether layer was then separated and dried by shaking in the cooling bath for five minutes with 40 g. of reagent grade calcium chloride. The aqueous layer was twice extracted with 100-cc. portions of ether, the extracts dried and combined with the above. After the addition of 440 cc. of absolute alcohol, the ether solution was distilled from a water-bath at about 60°; nitrogen was evolved. The resulting alcoholic solution was refluxed from an oil-bath for one hour, the solvent removed *in vacuo* and the residue treated at room temperature with absolute alcohol. The portion difficultly soluble (1.0 g.) was recrystallized from 80% alcohol, colorless hexagonal plates, m. p. 258.5–259.0°; this substance is possibly 4,5-dimethylenedihydro-aracil.

*Anal.* Calcd. for  $C_8H_{18}N_2O_2$ : C, 51.42; H, 5.75; N, 19.99. Found: C, 51.63; H, 5.88; N, 19.89.

The portion readily soluble in alcohol gave on evaporation 52 g. (55%) of crude crystalline *cis*-diurethan (V) which was suitable for conversion to *cis*-(VI). A sample was recrystallized from ethyl acetate, colorless needles, m. p. 101.5–102.0°.

The preparation of *trans*-(V) was carried out in a similar fashion except that the *trans*-(IV) dihydrochloride (100 g.) was dissolved in 200 cc. of water and the sodium nitrite solution was added maintaining the temperature of the reaction mixture at 18–20° (this slightly higher temperature was found, as the result of a series of experiments, to afford optimum yields). The reaction between the diazide and alcohol gave 2.2 g. of amorphous material difficultly soluble in absolute alcohol; this material, m. p. ca. 210°, could not be crystallized; on hydrolysis with alkali it yielded substantial amounts of *trans*-(VI). The average yield of alcohol soluble material was 57 g. (60%); it was used for conversion to *trans*-(VI). Pure *trans*-(V) was obtained by crystallization from aqueous alcohol, from which solvent it came out in both needles and cube-like crystals, m. p. 129.5–130.0°.

*Anal.* Calcd. for  $C_{10}H_{18}N_2O_4$ : C, 52.16; H, 7.88; N, 12.17. Found (*cis*): C, 52.24; H, 7.52; N, 12.05. Found (*trans*): C, 51.89; H, 7.51; N, 12.22.

*cis*- and *trans*-1,2-Diaminocyclobutanes (VI) from the Diurethans (V).—A solution of 250 g. of c. p. potassium hydroxide in 680 cc. of methanol was refluxed with 62 g. of crude *cis*-diurethan for one hour from a bath at 100°. The solvent was distilled off and the residue steam distilled from a bath at 170° until the distillate was neutral to litmus. The aqueous and methanolic distillates were

combined, acidified with c. p. concentrated hydrochloric acid and evaporated to dryness on the steam-bath, yield of crude hydrochloride nearly theoretical. The salt was dissolved in the minimum amount of water and the solution added dropwise to 100 g. of potassium hydroxide. The free base was isolated by continuous ether extraction; the ether extract after drying and distilling over sodium yielded 17.2 g. (77%) of diamine, b. p. 147°, b. p. 75° at 50 mm.,  $n_D^{20}$  1.4881,  $d_4^{20}$  0.9652.

The *trans*-diamine was prepared from crude *trans*-(V) in exactly the same manner; yield of crude hydrochloride theoretical. The continuous ether extraction required a longer time for completion than was necessary in the case of the *cis*-compound. From 62 g. of crude *trans*-(V), 14.4 g. (63%) of base was obtained, b. p. 151°, b. p. 74° at 50 mm.,  $n_D^{20}$  1.4837,  $d_4^{20}$  0.9490.

*Anal.* Calcd. for  $C_4H_{10}N_2$ : C, 55.77; H, 11.70; N, 32.53. Found (*cis*): C, 55.77; H, 11.90; N, 32.00. Found (*trans*): C, 55.59; H, 11.62; N, 31.77.

The diamines react readily with carbon dioxide<sup>22</sup>; the resulting ether insoluble addition compounds sublimed with decomposition, *cis*- at ca. 150°, *trans*- at ca. 110°. The following derivatives of *cis*- and *trans*-(VI) were made in the usual manner; the empirical formulas given were confirmed by analysis. Dibenzenesulfonamides,  $C_{16}H_{18}N_2O_4S_2$ : *cis*- m. p. 145.5–146.5° from alcohol, *trans*- m. p. 153.5–154.0° from alcohol. Dibenzamides from benzoyl chloride, base and aqueous alkali,  $C_{18}H_{18}N_2O_2$ : *cis*- m. p. 204.5–205.0° from absolute alcohol, *trans*- m. p. 245.5–246.0° from dioxane. Dipicrates from base with ethereal picric acid,  $C_{16}H_{18}N_8O_{14}$ : *cis*- insoluble in the usual solvents, crystallized by dissolving in pyridine and adding absolute alcohol, m. p. 255° dec.,<sup>23</sup> *trans*- m. p. 254° dec.,<sup>23</sup> from aqueous alcohol. Derivative from *trans*-diamine with phenyl isocyanate,  $C_{12}H_{20}N_4O_2$ : fine needles, m. p. 279–280° from dioxane-water; *trans*-oxalate,  $C_8H_{12}N_2O_4$ : prisms from aqueous alcohol, m. p. 268° dec.

*cis*- and *trans*-(VI) from the Dicarboxylic Acids (III).—In a 1-liter three-neck flask equipped with dropping funnel, mechanical stirrer, gas evolution indicator, and thermometer dipping into the liquid was placed 46 cc. of concentrated c. p. sulfuric acid. First, 20 g. (0.139 mole) of *cis*-(III) was added and then a solution of hydrazoic acid<sup>24</sup> in chloroform (from 32 g. of sodium azide and found by titration to contain 14.8 g. (0.335 mole) of hydrazoic acid) was added over a period of twenty-five minutes maintaining the temperature at about 40°. Heating was continued at this temperature for twelve hours; the reaction mixture was poured on ice, separated from chloroform and distilled to remove traces of this solvent. A solution of 180 g. of potassium hydroxide in water was added slowly with cooling and the mixture steam distilled at a bath temperature of about 160° (compare preceding section). The crude dihydrochloride, 16.5 g. (75%), was contaminated with a small amount of ammonium chloride. The free base was isolated as before, yield 4.2 g. (35%).

*trans*-Diamine was made by essentially the same procedure; a theoretical yield of crude dihydrochloride re-

(22) Compare *Chem. Zentr.*, **72**, II, 519 (1901).

(20) Procedure based on that used by Curtius [*J. prakt. Chem.*, [2] **52**, 221 (1895)] in the case of succindihydrazide.

(21) Higher temperatures gave poorer yields.

(23) Minimum temperature at which a fresh sample will decompose when placed for twenty seconds in a bath at this temperature.

(24) von Braun, *Ann.*, **490**, 125 (1931).

sulted. The yield of *trans*-(VI) was 7.3 g. (55%) from 22 g. of *trans*-(III).

These amines made directly from the dicarboxylic acids had the same physical constants and gave the same characteristic derivatives as the amines prepared by the Curtius degradation.

**Preparation of Cyclic Derivatives from *cis*-(VI).**—Although benzil reacted vigorously with *cis*-(VI), the reaction did not afford the expected derivative<sup>25</sup>; the only product isolated was tetraphenylpyrazine, needles from alcohol, m. p. 252.0–252.5° (analysis). Even when equivalent amounts of the reactants were brought together in ether solution at room temperature, under which conditions they react slowly, only tetraphenylpyrazine was isolated in pure form from the complex mixture of reaction products. The same substance was also formed by heating benzil together with *trans*-(VI).

Gaseous phosgene in excess was passed into an ethereal solution of *cis*-(VI) at 0°; the reaction proceeded rapidly with separation of solid. After evaporation of solvent the residue was dissolved in water, made alkaline and continuously extracted with ether. From the extract the cyclic urea derivative<sup>26</sup> was recovered as a crystalline solid together with unchanged *cis* diamine. The former was purified by sublimation at 100° at 2 mm. and recrystallization from a mixture of isopropyl ether and a small amount of absolute alcohol, colorless octahedra, m. p. 147.0–147.5°, difficultly soluble in ether, easily in alcohol or water.

*Anal.* Calcd. for C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>O: C, 53.55; H, 7.19; N, 24.99. Found: C, 53.63; H, 7.32; N, 25.10.

When *trans*-(VI) was treated in the same manner with phosgene, in addition to unchanged amine, only an amorphous insoluble product was isolated.

When excess of carbon disulfide was added to an alcoholic solution of *cis*-(VI), a white crystalline precipitate separated immediately. This salt<sup>27</sup> crystallized from aqueous alcohol, colorless plates, sintering with loss of hydrogen sulfide at about 152° and then melting at the melting point of the 2-thiol-4,5-dimethyleneimidazoline. The latter was prepared by evaporating an aqueous solution of the dithiocarbamate on the water-bath, colorless plates from water, m. p. 168.5–169.0°.

*Anal.* Calcd. for C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>S: C, 46.84; H, 6.29. Found: C, 46.80; H, 6.16.

When the *trans*-diamine was treated with carbon disul-

fide in the same manner, a similar precipitate of a dithiocarbamic acid internal salt formed, stable granular white crystals from hot water, sintering at 263°,<sup>28</sup> difficultly soluble in cold water or hot alcohol.

*Anal.* Calcd. for C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>S<sub>2</sub>: C, 37.01; H, 6.21; N, 17.27. Found: C, 36.77; H, 6.18; N, 16.81.

*cis*-Diamine (0.86 g. = 0.01 mole) and thioacetamide (0.75 g. = 0.01 mole) when stirred together at room temperature reacted exothermally with vigorous evolution of ammonia and hydrogen sulfide.<sup>28</sup> After the reaction had subsided, the mixture was heated for one-half hour at 80°. The product was taken up in 20 cc. of 12 *N* hydrochloric acid, the solution evaporated to dryness on a steam-bath, and the residue made alkaline and continuously extracted with ether. The pale yellow mass of needles thus obtained was sublimed at 90° and 2 mm. giving 0.82 g. of 2-methyl-4,5-dimethyleneimidazoline, colorless needles, m. p. 89.0–90.0° from benzene.

*Anal.* Calcd. for C<sub>6</sub>H<sub>10</sub>N<sub>2</sub>: C, 65.42; H, 9.15; N, 25.43. Found: C, 65.51; H, 9.03; N, 25.66.

The picrate crystallized from aqueous alcohol in yellow plates, m. p. 150.0–150.5°.

The reaction was carried out with *trans*-(VI) in the same manner; it was necessary to heat the mixture before gases were evolved. The product<sup>29</sup> was easily hydrolyzed with regeneration of *trans*-(VI) and was not investigated further.

## Summary

*cis*- and *trans*-1,2-cyclobutanedicarboxylic acids have been degraded by the Curtius and by the K. F. Schmidt method. These methods were shown to involve no change in configuration and to provide preparative routes to the diaminocyclobutanes.

PASADENA, CALIFORNIA

RECEIVED JULY 22, 1942

(28) The preparation of imidazolines by the interaction of a thioamide with a diamine has been limited to a few instances (Forssell, *Ber.*, **25**, 2132 (1892); McClelland and Warren, *J. Chem. Soc.*, 2621 (1929); see also U. S. Patent 2,252,721, *Chem. Abs.*, **35**, 7658 (1941)). In view of the current interest in imidazoline chemistry, it may be pointed out that the reaction is quite generally applicable, proceeds readily under mild conditions (advantage over usually employed methods) and affords good yields of the desired products which may in many instances be isolated directly from the reaction mixture by sublimation. Caution! Many imidazolines readily undergo hydrolytic fission, Aspinall, *J. Org. Chem.*, **6**, 895 (1941).

(29) Compare Schlatter, *THIS JOURNAL*, **64**, 2722 (1942).

(25) Compare Mason, *Ber.*, **20**, 268 (1887).

(26) Compare Einhorn and Bull, *Ann.*, **295**, 216 (1897).

(27) Compare Hofmann, *Ber.*, **5**, 240 (1872).