

TABLE I  
 PREPARATIONAL DATA

|          | Taken,<br>g. | Aldehyde                   | Taken,<br>g. | Product  | Yield,<br>g. | KCN,<br>g. | Hours<br>heating | Cc. of<br>alcohol |
|----------|--------------|----------------------------|--------------|--|--------------|------------|------------------|-------------------|
| Benzoin  | 4.24         | Dimethylam-<br>inobenz-    | 5.96         | Dimethylam-<br>inobenzoin <sup>4</sup>         | 9.18         | 3.0        | 3.0              | 20                |
| Benzoin  | 4.24         | Anis-                      | 5.44         | Benzanisoin <sup>5</sup>                       | 7.36         | 4.0        | 2.0              | 20                |
| Benzoin  | 4.24         | Furfural                   | 3.84         | Benzfuroin <sup>5</sup>                        | 3.98         | 3.0        | 1.5              | 20                |
| Benzoin  | 4.24         | Piperonal                  | 6.00         | Benzpiperoin <sup>2</sup>                      | 2.16         | 2.0        | 0.5              | 30                |
| Piperoin | 3.00         | Dimethylam-<br>inobenz-    | 2.98         | Dimethylamino-<br>benzpiperoin                 | 2.12         | 2.0        | 3.0              | 15                |
| Piperoin | 3.00         | <i>o</i> -Chloro-<br>benz- | 2.82         | <i>o</i> -Chlorobenz-<br>piperoin <sup>6</sup> | 2.05         | 2.0        | 3.0              | 15                |
| Piperoin | 6.00         | Benz-                      | 4.24         | Benzpiperoin <sup>2</sup>                      | 1.29         | 4.0        | 2.0              | 30                |
| Furoin   | 3.84         | Dimethylam-<br>inobenz-    | 5.96         | Dimethylamino-<br>benzfuroin <sup>5</sup>      | 5.77         | 3.0        | 1.5              | 20                |
| Furoin   | 3.84         | Benz-                      | 4.24         | Benzfuroin <sup>5</sup>                        | 4.06         | 2.0        | 0.16             | 20                |

<sup>4</sup> Staudinger, *Ber.*, **46**, 3535 (1913).

<sup>5</sup> Fischer, *Ann.*, **211**, 214 (1882).

<sup>6</sup> Buck and Ide, *THIS JOURNAL*, **52**, 220 (1930).

### Summary

A general method for demonstrating the reversibility of the benzoin condensation is described, involving the preparation of mixed benzoin from simple benzoin. Some of the consequences of the reversibility are discussed. A new mixed benzoin is described.

TUCKAHOE, NEW YORK

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

## STEREOCHEMISTRY OF N,N'-DIPYRRYLS. RESOLUTION OF N,N',2,5,2',5'-TETRAMETHYL-3,3'-DICARBOXYDIPYRRYL. XVI<sup>1</sup>

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The resolution of N,2-carboxyphenyl-2,5-dimethyl-3-carboxypyrrole<sup>1b</sup> (I) demonstrated that optical isomerism which was possible in properly substituted diphenyls, due presumably to restricted rotation of the rings, may also occur in substituted N-phenylpyrroles. This indicates the probability of optical isomerism in other dicyclic compounds such as in properly substituted dipyrlyls. The more important general types of this class of compounds which from analogy to the diphenyls might exhibit isomerism may be represented by the Formulas II, III, IV.

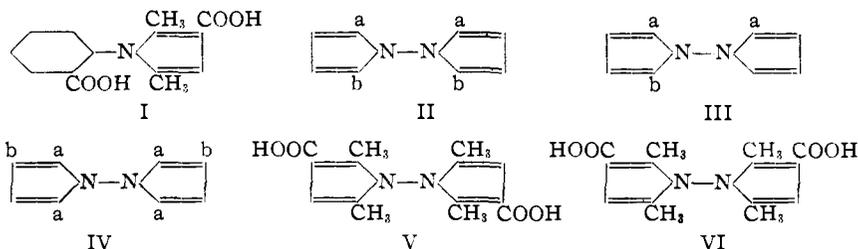
The investigation described in this communication has involved the

<sup>1</sup> For the previous papers in this series see (a) Shildneck and Adams, *THIS JOURNAL*, **53**, 343 (1931); (b) Bock and Adams, *ibid.*, **53**, 374 (1931).

<sup>2</sup> This communication is an abstract of a portion of a thesis submitted by Chin Chang in partial fulfillment of the requirements for the degree of Doctor of Philosophy in chemistry.

preparation and resolution of a  $N,N'$ -dipyrrolyl of type III, namely,  $N,N'$ -2,5,2',5'-tetramethyl-3,3'-dicarboxydipyrrolyl, the two enantiomorphs of which might be represented by Formulas V and VI.

These are written as if the three valences of each nitrogen were in a single plane, upon which assumption the compounds would resemble diphenyl in structure. It is probable, also, that under such conditions restricted rotation in the dipyrrolyl molecules would conform more or less closely to that of the diphenyl series.



On the other hand, on the assumption of a tetrahedral structure for nitrogen, the geometric structures of the phenylpyrroles and the  $N,N'$ -dipyrrolyls will be quite different from the diphenyls. In the latter compounds there is a single axis for the two rings, but in the phenylpyrroles and the dipyrrolyls this would not be true. The formula for phenylpyrrole is illustrated by (VII) and a dipyrrolyl would be of a similar character excepting that the angle between the two pyrrole rings in the molecule would be considerably different from the angle between the benzene and the pyrrole rings in phenylpyrrole. It might well be expected in molecules of these types that other conditions of substitution would affect restricted rotation between the rings.

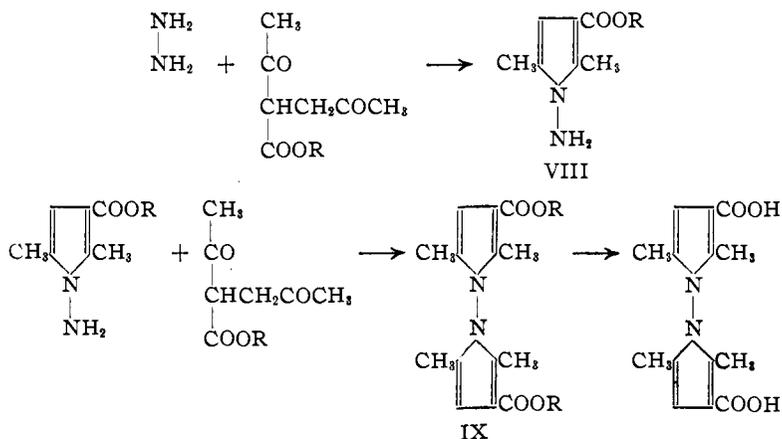


In fact, upon the assumption of a regular tetrahedral structure for the nitrogen atom, it is difficult to see how *ortho* substituted groups in the pyrrole rings of a dipyrrolyl would interfere with each other at all.

Other possibilities for isomerism may occur in these molecules that do not have a single axis for the two rings. If one ring is unable to rotate on the C-N or the N-N axis to the other side of the second ring, conditions exist which are not possible in the diphenyl series. Whereas in diphenyls the molecules must have restricted rotation between the rings and in addition each ring must be asymmetrically substituted in itself to allow the possibility of mirror images, in a phenylpyrrole or dipyrrolyl restricted rotation and asymmetry in only one of the rings would be necessary in order to make possible optical activity. Such molecules may readily be produced and some light should thus be thrown on the structures of the phenylpyrroles and dipyrrolyls from the results of the investigation now under way.

The racemic  $N,N',2,5,2',5'$ -tetramethyl-3,3'-dicarboxydipyrpyl was readily resolved through the brucine salt and the two optically active forms (V and VI) obtained in a pure state. They proved to be very resistant to racemization under ordinary conditions. After twenty-four hours of boiling in pyridine no change in rotation occurred. Even after boiling for eighty-four hours in 0.1  $N$  sodium hydroxide the racemization was only partial. Insolubility in all ordinary solvents except pyridine limited the study of the ease of racemization.

The compound  $N,N',2,5,2',5'$ -tetramethyl-3,3'-dicarboxydipyrpyl has already been described by Korschun,<sup>3</sup> who obtained it as a by-product in the condensation of hydrazine with 3-carboxy-2,5-dimethylhexadione in alcohol solution. It was found, however, that it could be produced in quantity more readily by using a slightly different procedure. Hydrazine was first condensed with 3-carboethoxy-2,5-dimethylhexadione in alcohol and acetic acid with the formation of  $N$ -amino-2,5-dimethyl-3-carboethoxy-pyrrole (VIII). This latter substance was then condensed again with 3-carboethoxy-2,5-dimethylhexadione with the formation of the substituted dipyrpyl (IX).



Outside of the fact that the dibrucine salt tended to hydrolyze readily in the presence of solvents containing any water, there was nothing unusual to mention in connection with the resolution of this compound into its active forms.

The results of this investigation offer additional evidence that optical isomerism due to restricted rotation between rings may be expected in many, if not in all, heterocyclic and alicyclic types that are semi-aromatic in character where the proper number and kind of groups are substituted in the ortho positions to the linkage between the rings.

<sup>3</sup> Korschun, *Ber.*, 37, 2183 (1904).

### Experimental

**N,N',2,5,2',5'-Tetramethyl-3,3'-dicarboethoxydipyrrol.**—A solution of 15 g. of N-amino-2,5-dimethyl 3-carboethoxypyrrole (Korschun)<sup>3</sup> in 200 cc. of absolute methyl alcohol was heated with 15 g. of 3-carboethoxy-2,5-dimethylhexadione in a 500-cc. flask fitted with a reflux condenser for four hours on a steam-bath. The solvent was then evaporated from the reaction mixture. A thick oily substance was obtained; yield 26 g. (94% of the theoretical).

**N,N',2,5,2',5'-Tetramethyl-3,3'-dicarboxydipyrrol.**—A mixture of 26 g. of N,N',2,5,2',5'-tetramethyl-3,3'-dicarboethoxydipyrrol with 70 cc. of 10% alcoholic potassium hydroxide was heated for two hours on a steam-bath. Upon acidifying the resulting solution with a little hydrochloric acid, a brownish precipitate was obtained. The product was filtered and washed with water. This was then dissolved in about 400 cc. of absolute methyl alcohol and refluxed for half an hour with 6 g. of decolorizing charcoal. After filtration, sufficient water was added until a precipitate just appeared. Upon standing the dipyrrol separated as a white precipitate which upon drying amounted to 18 g. (84% of the theoretical). It was purified by crystallizing from absolute methyl alcohol until it had a constant melting point of 278–280°.

It is slightly soluble in ethyl acetate, ethyl alcohol, benzene and chloroform and somewhat more soluble in absolute methyl alcohol and acetone.

*Anal.* Calcd. for C<sub>14</sub>H<sub>16</sub>O<sub>4</sub>N<sub>2</sub>: mol. wt., 276; N, 10.11. Found: mol. wt., 279; N, 9.96.

**Resolution of N,N',2,5,2',5'-Tetramethyl-3,3'-dicarboxydipyrrol.**—A solution of 20 g. of brucine in 400 cc. of absolute methyl alcohol was heated to its boiling point and 7 g. of powdered N,N',2,5,2',5'-tetramethyl-3,3'-dicarboxydipyrrol was added slowly with stirring. After standing for several hours at 0°, the salt which separated was filtered. The first fraction thus obtained which amounted to 12.7 g. was crystallized from absolute methyl alcohol three times until a constant rotation was obtained; melting point 153–157°.

*Rotation.* *d*-Salt, 0.1024 g. made up to 25 cc. with pyridine at 20° gave  $\alpha_D$  -0.60;  $l$  = 2;  $[\alpha]_D^{20}$  -73.2.

*Anal.* Calcd. for C<sub>60</sub>H<sub>68</sub>N<sub>6</sub>O<sub>12</sub>: N, 7.87. Found: N, 7.76.

The more soluble fraction obtained in solution as a filtrate from the less soluble salt was evaporated part way to dryness and again allowed to cool. Any crystalline material which separated was filtered and consisted of a mixture of the two salts, though primarily of the less soluble. It was necessary to concentrate to dryness before the more soluble salt was obtained. It then separated from the methyl alcohol as a gum which on long standing in a desiccator solidified. It was found impossible to recrystallize this material so that in the crude form a sample was weighed out and a rotation taken. The rotation undoubtedly is not the maximum one for the salt.

*Rotation.* *l*-Salt, 0.1550 g. made up to 50 cc. with pyridine at 20° gave  $\alpha_D$  -0.51;  $l$  = 2;  $[\alpha]_D^{20}$  -82.3°.

The *l*-salt in this crude form melted at 293–304°. It turned dark at 241°.

***d*- and *l*-N,N',2,5,2',5'-Tetramethyl-3,3'-dicarboxydipyrrol.**—The active acids were liberated from the individual salts by suspending in water and treating with hydrochloric acid. A suspension of 4 g. of the less soluble salt in 100 cc. of water was treated with 4 cc. of concentrated hydrochloric acid and thoroughly stirred. The solid acid which precipitated was filtered and recrystallized to a constant melting point from absolute methyl alcohol. Melting point, 218–219°.

*Rotation.* *d*-Acid, 0.1817 g. made up to 25 cc. with pyridine at 20° gave  $\alpha_D$  +0.40;  $l$  = 2;  $[\alpha]_D^{20}$  +27.5.

*Anal.* Calcd. for C<sub>14</sub>H<sub>16</sub>O<sub>4</sub>H<sub>2</sub>: C, 60.87; H, 5.85. Found: C, 61.03; H, 6.10.

The *l*-acid was obtained in a similar manner from the crude soluble salt. The free acid was recrystallized from absolute methyl alcohol; melting point 220–221°.

*Rotation.* *l*-Acid, 0.1544 g. made up to 25 cc. with pyridine at 20° gave  $\alpha_D -0.31$ ;  $l = 2$ ;  $[\alpha]_D^{20} -25.1$ .

**Racemization Experiments.**—A solution of 0.1817 g. of *d*-acid made up to 25 cc. with pyridine at 20°,  $\alpha_D +0.40$ ,  $l = 2$ ,  $[\alpha]_D^{20} +27.5$ , was refluxed for twenty-four hours. No change in initial rotation was observed.

A solution of 0.1990 g. of *d*-acid in 50 cc. of 0.1 *N* sodium hydroxide gave an initial rotation of  $\alpha_D +0.19$ ;  $l = 2$ ;  $[\alpha]_D^{20} +23.9$ ; upon boiling for eighty-four hours the rotations were as follows: nine hours,  $\alpha_D +0.14$ ,  $l = 2$ ,  $[\alpha]_D^{20} +17.6$ ; forty-eight hours,  $\alpha_D +0.12$ ,  $l = 2$ ,  $[\alpha]_D^{20} +15.1$ ; seventy-two hours,  $\alpha_D +0.07$ ,  $l = 2$ ,  $[\alpha]_D^{20} +8.8$ ; eighty-four hours,  $\alpha_D +0.06$ ,  $l = 2$ ,  $[\alpha]_D^{20} +7.5$ .

### Summary

1. *N,N',2,5,2',5'*-Tetramethyl-3,3'-dicarboxydipyrrol has been prepared by condensing *N*-amino-2,5-dimethyldicarboethoxypyrrole with 3-carboethoxy-2,5-dimethylhexadione.

2. The product was resolved through the brucine salt and the active forms were found to be unusually resistant to racemization.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

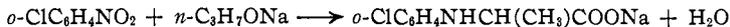
## THE REDUCTION OF AROMATIC NITRO AND NITROSO COMPOUNDS WITH SODIUM ALCOHOLATES. II.

BY F. B. DAINS AND W. O. KENYON

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The reduction of aromatic nitro compounds with sodium or potassium hydroxide in alcohol solution or with sodium alcoholates has been studied by a number of investigators from the time of Mitscherlich to the present.<sup>1</sup> Under various conditions there have been obtained amines, azoxybenzene, azobenzene and in the case of *p*-nitrotoluene stilbene derivatives. In addition, Suter and Dains have found that the reduction of *o*-halogen nitrobenzenes with sodium propylate or butylate gave an unexpected product, a substituted amino acid.<sup>2</sup>



<sup>1</sup> E. Mitscherlich, *Ann.*, **12**, 311 (1834); Rasenack, *Ber.*, **5**, 364 (1872); Zinin, *J. prakt. Chem.*, [I] **36**, 98 (1845); Klinger, *Ber.*, **15**, 865 (1882); Schultz and Smith, *Ann.*, **207**, 328 (1881); Holleman, *Rec. trav. chim.*, **35**, I (1915); Blom, *Helv. Chim. Acta*, **4**, 297 (1921); Fry and Cameron, *THIS JOURNAL*, **49**, 864 (1927); Heumann, *Ber.*, **5**, 911 (1872); Brand, *J. prakt. Chem.*, [II] **68**, 208 (1903); Richardson, *J. Chem. Soc.*, 522 (1926); McMasters and Magill, *THIS JOURNAL*, **50**, 3038 (1928); Perkin, *J. Chem. Soc.*, **37**, 546 (1880); Goldschmidt, *Ber.*, **11**, 1624 (1878); Buchka and Schachtebeck, *ibid.*, **22**, 834 (1889); Schmidt, *ibid.*, **32**, 2919 (1899); Green, Davies and Horsfall, *J. Chem. Soc.*, **91**, 2076 (1907); Brühl, *Ber.*, **37**, 2066 (1904); Lyons and Pleasant, *ibid.*, **62**, 1723 (1929).

<sup>2</sup> Suter and Dains, *THIS JOURNAL*, **50**, 2733 (1928).