

acid but the formula was not proved by analysis.<sup>1</sup> No yield was given of this acid and it was not clear from the description in his paper that the 145° melting acid was used for pyrogenic decomposition. In his preparation of the tribasic acid through tiglic and sodium enol malonic esters, Ray obtained it as a sirup from which apparently he could obtain the 134° melting dicarboxylic acid more readily than from the 145° melting acid. It is therefore difficult to understand the reference in his letter of "necessity to purify before decomposition." The acid melting at 134° was described as  $\alpha,\beta,\gamma$ -trimethylglutaric acid, although no analyses of this material are given. We, therefore, cannot attach the importance that Ray does to this substance of unknown composition, obtained from an impure source.

With respect to the second objection, the validity of the method is a well established fact. The stereomeric poly-alkyl dicarboxylic acids do not form anhydrides with equal facility, or of equal stability, and we refer Dr. Ray to the literature of these acids [Perkin and Bone, *J. Chem. Soc.*, 69, 264 (1896); Thorpe and Young, *ibid.*, 83, 358 (1903), and others].

Since we used this method in the separation of the  $\alpha,\beta,\gamma$ -trimethylglutaric acids, our products were described as *cis* and *trans* to indicate their origin and relative ease of anhydride formation. It was not relevant to our investigation to separate the possible stereomeric forms of  $\alpha,\beta,\gamma$ -trimethylglutaric acid; it was sufficient for us to obtain a pure imide, m. p. 90°, and an acid, m. p. 125°, as reference compounds and to indicate further the existence of a *trans* acid form.

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#### STEREOCHEMISTRY OF DERIVATIVES OF DIPHENYL AND ANALOGS

*Sir:*

Apparently the first suggestion that stereoisomerism of the type observed in the diphenyl series might also occur among binuclear heterocyclic aromatic substances is due to Kermack and Slater,<sup>1</sup> who attempted the resolution of 3-*o*-nitrophenyl-indole-2-carboxylic acid. A recent publication by Steele and Adams<sup>2</sup> describes the attempted resolution of certain phenylpyridine compounds.

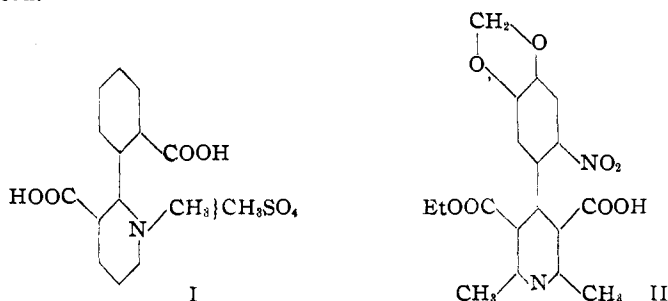
<sup>1</sup> Ray gives no C and H analysis of this acid. Using very small quantities of material he showed by analysis of the silver salt that the silver content agreed with the formula of a tricarboxylic acid  $C_8H_{14}O_6$ , but titration with 0.1 *N* alkali indicated a dicarboxylic acid  $C_8H_{14}O_4$ . Analysis of the silver salt and titration could only indicate the equivalent of the acid. These conflicting analyses cannot indicate whether the acid was methylated; that is, whether the acid was  $C_8H_{14}O_6$  or  $C_8H_{12}O_6$ .

<sup>1</sup> Kermack and Slater, *J. Chem. Soc.*, 36 (1928).

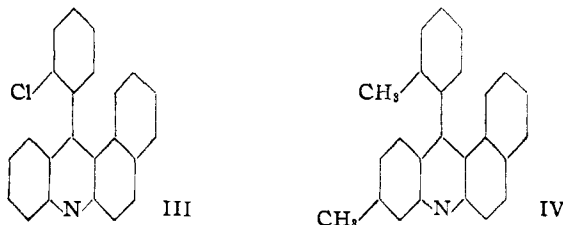
<sup>2</sup> Steele and Adams, *THIS JOURNAL*, 52, 4528 (1930).

An extensive investigation of such heterocyclic substances as might be expected to exhibit stereoisomerism of diphenyl type has been in progress in these laboratories for some time, but owing to failure to obtain the substances examined in enantiomorphous forms up to the present, publication of results, with the exception of an introductory paper by Chalmers, Lions and Robson,<sup>3</sup> has been so far withheld.

In the 2-phenylpyridine series and the 2-phenylquinoline series attempts have been made to provide a "blocking group" by conversion of the tertiary nitrogen atom into a quaternary salt. Thus, 2-(-*o*-carboxyphenyl)-3-carboxypyridine methosulfate (I) has been examined, but its resolution not effected.



Derivatives of 4-phenylpyridine such as (II) have been prepared by the Hantzsch synthesis, and attempts at resolution are in progress. It is worthy of note in this connection that ortho-substituted benzaldehydes react least readily in the Hantzsch synthesis.<sup>4</sup> In the isoquinoline series 1-(-*o*-chlorophenyl)-isoquinoline methiodide and ethiodide, and 1-(-*o*-tolyl)-isoquinoline methiodide and ethiodide have been prepared and converted into the corresponding salts of optically active acids, but these are apparently homogeneous. The acridine compounds (III) and (IV) have also been prepared and examined but not separated into enantiomorphs.

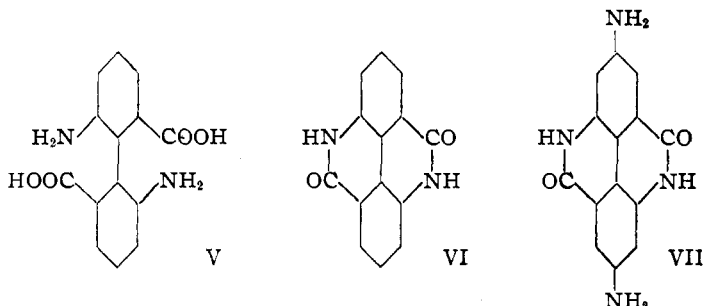


This consistent failure to resolve a compound of the phenylpyridine series suggests that the conditions there obtaining are different from those in the diphenyl series, probably owing to the definitely polar character of

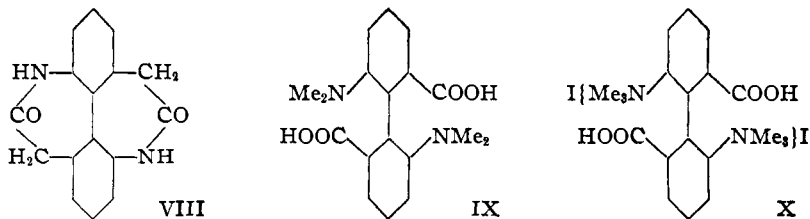
<sup>3</sup> Chalmers, Lions and Robson, *J. Roy. Soc. New South Wales* (1930).

<sup>4</sup> Hinkel and Madel, *J. Chem. Soc.*, 750 (1929).

the pyridine nitrogen atom. Undoubtedly, there would be a powerful attraction between this atom and an ortho carboxyl of the benzene ring, leading to pronounced molecular distortion. As yet, the resolution of a derivative of diphenyl having strongly positive groups in the 2,2'-positions and strongly negative groups in the 6,6'-positions has not been effected. 2,2'-Diamino-6,6'-dicarboxydiphenyl (V) passes immediately on its formation into the dilactam (VI).<sup>5</sup> Presumably, in this substance both pyridone rings lie in the same plane as the benzene rings, though this has not definitely been established.

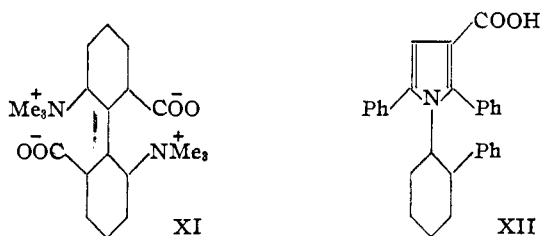


At present the optical homogeneity of (VII) is under examination. It is also proposed to attempt the preparation and resolution of ring homologs of (VI), *e. g.*, the dilactam (VIII) in which the benzene rings should lie out of one plane, two configurations thus being possible. Further attempts to resolve 2,2'-tetramethyldiamino-6,6'-dicarboxydiphenyl (IX) and 2,2'-hexamethyldiamino-6,6'-dicarboxydiphenyl dimethiodide (X) and the corresponding betaine (XI) are in progress. The behavior of all these substances may shed some light on the phenomenon in the phenylpyridine series.



Finally, the examination of certain phenylpyrroles and phenylindoles is in progress. According to the obstacle theory it is to be expected that in such binuclear systems the smallest groups which would be effective in preventing free rotation of the nuclei about their common axis must be larger than in the diphenyl series. Hence, the first example chosen for study which is expected to be resolvable is 1-(*o*-xenyl)-2,5-diphenylpyrrole-3-carboxylic acid (XII).

<sup>5</sup> Cf. Kenner and Stubbings, *J. Chem. Soc.*, 119, 593 (1921).



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### THE CRYSTAL FORM OF NICKEL OXIDES

*Sir:*

In making adsorption measurements of carbon dioxide on nickel oxide, it was found by one of us<sup>1</sup> that the adsorptive properties of the oxide varied quite markedly for different modes of heat treatment.

The nickel oxide was prepared by oxidation of suspended nickelous hydroxide with chlorine gas in basic solution. The black precipitate of the oxide was electrolyzed free of alkali and dried. One sample was out-gassed several times at 285°, while the other was not subjected to a temperature of more than 110°.

The first preparation was the poorer adsorbent for carbon dioxide. The adsorption was carried out at 56.5° and the amounts adsorbed were in the approximate ratio of 1:2.5.

This difference of behavior, which was unlikely due to sintering, since the overheated form had rather smaller particle size as indicated by the line-width of the x-ray diagrams referred to below, also could not be explained on the basis of chemical differences, since in the Bunsen test for higher oxides, only traces of such could be found in either case. Both samples corresponded to nickelous oxide.

The substances were then subjected to x-ray analysis by means of the Debye-Scherrer-Hull method.

The overheated oxide corresponded exactly to the previously reported structure for nickelous oxide, being face-centered cubic. The edge of the unit cube was found to be 4.14 Å. (uncorrected), which corresponds to 4.17 Å. as given by the "International Critical Tables."

The structure of the nickelous oxide which had not been heated above 110° was quite different. Although also cubic, the edge of the unit cube was 4.64 Å. (uncorrected). The density was determined as 4.8 as compared to 6.69, given as the density of the ordinary nickelous oxide (Landolt-Börnstein "Tabellen"). The number of molecules in the unit cell

<sup>1</sup> O. G. Bennett, "Thesis," The Johns Hopkins University, 1930.