227. *Studies on Hydrogen Cyanide. Part XII. The Asymmetry of the Tetrapolymer of Hydrogen Cyanide.*

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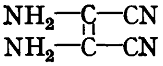
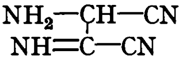
Evidence for the views expressed by Hinkel, Richards, and Thomas (J., 1937, 1432) for the asymmetric structure of the tetrapolymer of hydrogen cyanide has now been obtained. From the *salt* which the polymer forms with δ-camphorsulphonic acid one of the two diastereoisomerides, possessing a strong lævorotation, has been obtained by a process of partial solution. The two diastereoisomerides are mutually interconverted by simple solution, this conversion becoming predominant in one direction at higher temperatures. The active salt is readily hydrolysed by water, the free base so obtained being inactive owing to its racemisation on liberation from its salt.

The condensation of the tetrapolymer of hydrogen cyanide with glyoxal to form a dicyanopyrazine led Gryszkiewicz-Trochimowski (*Rocz. Chem.*, 1928, **8**, 165) to assign to the polymer the diaminomaleinitrile structure (I). On the other hand, Hinkel, Richards, and Thomas (J., 1937, 1432; cf. Hinkel, J., 1939, 492) found that in its behaviour with hydrogen chloride, benzaldehyde, and acetic anhydride, the tetrapolymer did not display the characteristic properties of an aliphatic diamine. They assigned to the compound the aminoiminosuccinonitrile structure (II) which they considered was alone capable of explaining all its reactions.



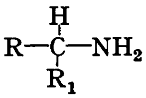
$$\begin{array}{c} \mathrm{NH_2{-}C{-}CN} \\ \| \\ \mathrm{NH_2{-}C{-}CN} \end{array}$$

(I.)



$$\begin{array}{c} \mathrm{NH_2{-}CH{-}CN} \\ | \\ \mathrm{NH{=}C{-}CN} \end{array}$$

(II.)



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{R{-}C{-}NH_2} \\ | \\ \mathrm{R_1} \end{array}$$

(III.)

The outstanding difference between these two structures lies in the asymmetric character of the latter, and if the compound has this constitution it should exhibit optical activity. Evidence for this has therefore been sought.

In the present investigation, although the active forms of the free base have not been isolated, an optically active *diastereoisomeride* possessing a strong lævorotation has been obtained with δ-camphorsulphonic acid. This fact can only be explained on the premise that the base component must possess a high lævorotation, and this was confirmed by making comparative readings with solutions in pyridine of (*a*) an equivalent of free δ-camphorsulphonic acid, (*b*) a mixture of the equivalent amounts of the δ-acid and inactive base, and (*c*) an equivalent amount of the salt prepared by direct union of the inactive base with the δ-acid without crystallisation, so that no separation could have occurred. In these three cases the optical rotations were identical and were therefore due to the δ-acid alone.

The resolution of the tetrapolymer presented some unusual features: not only are the two active diastereoisomerides mutually interconverted by simple solution, but also this inversion takes place predominantly in one direction with increase of temperature, to form the *l*-diastereoisomeride.

Asymmetric transformations are well known (*Ann. Reports*, 1933, **30**, 261; 1939, **36**, 247), and have been classified by Kuhn (*Ber.*, 1932, **65**, 49) into two orders. According to him, a "first order" is one in which the two interconvertible diastereoisomerides do not separate from solution, whereas in the "second order" only one diastereoisomeride separates from solution.

The diastereoisomerides of the tetrapolymer of hydrogen cyanide cannot be relegated to either order, since, although crystallisation from cold solution gives no separation, yet a very slight separation can be obtained by crystallisation from hot saturated solutions.

Treatment of the racemate with insufficient cold solvent for complete solution effects a partial separation of the diastereoisomerides, since the m. p. of the undissolved solid is considerably raised. This process of partial solution of the solid mixture of isomerides, if carried out at a higher temperature, results in a complete conversion of the undissolved solid into the less soluble *l*-diastereoisomeride. In these circumstances a greater dissolution of the *d*-compound occurs. The shift in equilibrium in solution, which occurs with rise in temperature, causes the conversion of the *d*-component into the more insoluble *l*-component, which is then deposited. This process continues until all the *d*-component has been converted into the *l*-component.

When the camphorsulphonate of the base is heated in alcoholic solution for any appreciable length of time, considerable darkening of the solution occurs owing to the partial decomposition of the base portion of the salt, since the free base behaves similarly when in aqueous or alcoholic solution.

In aqueous solutions the camphorsulphonate undergoes hydrolysis into the free acid and base, the latter separating from the solution as colourless crystals. The base can also be completely liberated from its salt by means of dilute alkali, the base so liberated being optically inactive. In pyridine solution no dissociation occurs, and it is remarkable that even in a 10% aqueous solution of pyridine no dissociation apparently takes place and, although the rotation is less than in pure pyridine, the rotations of the controlled solutions are also proportionately lowered.

That the liberated base from the camphorsulphonate should be inactive was not wholly unexpected, since it has been shown (Pope and Harvey, J., 1901, **79**, 85) that in all those cases where racemisation of the liberated base occurred, the base contained the grouping (III), which is present in the tetrapolymer (II).

EXPERIMENTAL.

The crude tetrapolymer, obtained by extraction of the black polymerised product of hydrogen cyanide, was purified by crystallisation from *iso*butyl alcohol (charcoal) and finally from hot amyl alcohol, being obtained as white needles, m. p. 184° (decomp.). [The majority of previous workers record 180° but Fialkoff (*Zentralbl.*, 1926, **41**, 1209) recorded 182° and Hinkel, Richards, and Thomas (*loc. cit.*) give 181°.]

Preparation of Aminoiminosuccinonitrile δ-Camphorsulphonate.—To a hot solution of the tetrapolymer (1·0 g.; 1 mol.) in dry ethyl acetate (25 c.c.) a hot solution of δ-camphorsulphonic acid (2·2 g.; 1 mol.) in ethyl acetate (40 c.c.) was quickly added with stirring. The salt was immediately precipitated as white micaceous plates. After cooling, these were filtered off, washed with a little cold ethyl acetate, and dried in a vacuum (yield almost quantitative). The solid melts sharply with decomposition at a temperature between 176° and 182° according to the initial temperature of the reactant solutions. Repeated crystallisation of the salt from alcohol yielded crystals having m. p.'s varying between 176° and 182°, whereas by fractional crystallisation from a hot saturated solution in alcohol, it was possible to obtain crystals having a m. p. as high as 186°.

Conversion of the Racemate into the l-*Diastereoisomeride.*—1 G. of the camphorsulphonate (m. p. 176—182°) was boiled under reflux with ethyl acetate (100 c.c.). At first the boiling proceeded gently, the solid gradually became granular, and when the change was complete (1—1½ hrs.) the solution bumped violently. At this stage the mixture was filtered whilst hot, and the solid after being quickly washed with a little cold ethyl acetate was dried in a vacuum; m. p. 237° (decomp.) (Found: S, 9·35; N, 16·7. $C_{14}H_{20}O_4N_4S$ requires S, 9·4; N, 16·5%). The *salt* is fairly soluble in acetonitrile and somewhat less soluble in propionitrile in the hot, and when crystallised from these solvents the partly racemised solids so obtained have m. p.'s varying between 190° and 226°. These lower-melting solids can readily be reconverted into the higher-melting solid (237°) by boiling with ethyl acetate as described above.

Measurements of Optical Rotations.—The camphorsulphonate of the base is very soluble in pure pyridine and also in dilute aqueous pyridine solution. In order to obtain comparable polarimetric readings, solutions were made containing 1 g. of the active salt (corresponding to 0·6823 g. of camphorsulphonic acid and 0·3176 g. of the polymer) in 50 c.c. of the solvent. Similarly, control solutions were made of (*a*) the same concentration of the free active acid, (*b*) a mixture of the acid and base corresponding to 1 g. of the salt, (*c*) 1 g. of unresolved salt (m. p. 176°), (*d*) 1 g. of partially resolved salts (m. p. between 176° and 237°). In all cases the solutions were filtered into the 40-cm. polarimeter tube used for the observations.

Polarimetric Readings.

Substance.	Rotations in pyridine at 19°.	Rotations in water + 10% pyridine at 19°.
Resolved *l*-salt, m. p. 237°	−42·4°	−29·23°
Partially resolved salt, m. p. 224°	−36·4	—
,, ,, ,, m. p. 207°	−15·5	—
,, ,, ,, m. p. 190°	+ 1·83	—
Unresolved salt, m. p. 176°	+ 2·1	+ 1·0
δ-Camphorsulphonic acid	+ 2·1	+ 1·0
δ-Acid + polymer	+ 2·07	+ 1·0

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