Rearrangement of *cis*-Caronic Acid to *trans*-Caronic Acid

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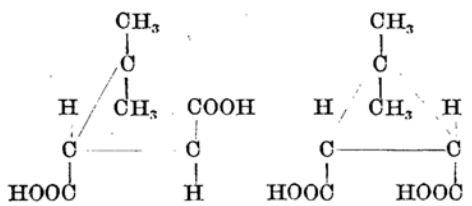
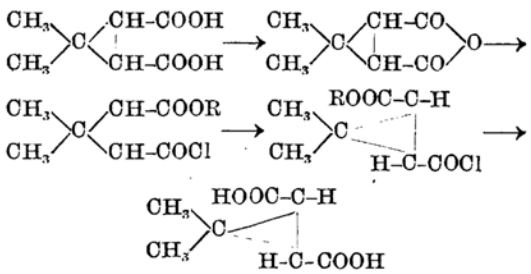
There are many studies on the rearrangement from *cis*-compounds to *trans*-ones and *trans*-ones to *cis*-ones, but few can be found on the rearrangement of compounds which contain cyclopropane ring.

It has been known with caronic acid that its *trans* form rearranges to *cis* anhydride by heating the former with thrice its quantity of acetic anhydride at 220° in the sealed tube.[1]



trans-Caronic acid *cis*-Caronic acid

However, in any report it can not be discovered that the *cis*-acid rearranges to the *trans*-one. Like in the case of geometric isomerism of unsaturated compounds, the *trans*-acid would be more stable than the *cis*-one and the rearrangement of *cis* → *trans* would take place. However, in the case of this caronic acid, as the two carboxyl groups are free, they may form the stable anhydride, and the rearrangement may not result. Therefore, it may be the matter of course that the *cis*-acid rearranges to *trans*-acid when it is heated after being converted to half ester which can not become intramolecular anhydride.



When the writer studied on caronic acid for other purpose, it was found that when isoamyl ester chloride of *cis*-caronic acid is heated, it rearranges to *trans*-acid as shown above. In the case of free *cis*-caronic acid, however, even if there was water enough to prevent free acid to convert its anyhdride, the rearrangement from *cis* to *trans* did not perform, when the

(1) Perkin and Thorpe, *J. Chem. Soc.*, **75**, 52.

mixture of water and free *cis*-acid was heated at 200° for seven hours in a sealed tube.

It is interesting that the conversion occurs only in the case of the half ester acid chloride.

Experimental

***cis*-Caronic Anhydride.**—*trans*-Caronic acid (m.p. 212°, 1 part), totally synthesized, is heated with acetic anhydride (3 parts) at 220° in a sealed tube for six hours. Then it was distilled and the distillate boiling at *ca.* 143° (20 mm.) was collected. It crystallized soon. It was recrystallized from dry ether and showed m.p. 56°. Boiled with water, *cis*-caronic acid, m.p. 174°, was obtained.

Isoamyl Hydrogen *cis*-Caronate.—Twenty grams of caronic anhydride, 13 g. of isoamyl alcohol and 15 g. of benzene were mixed and the mixture was refluxed on a water-bath for three hours. After cooling, it was extracted with 10% sodium carbonate solution. After the extract was washed with ether, it was acidified with hydrochloric acid. Separating oil was extracted with ether. The ether extract was washed with water and dried on the anhydrous sodium sulfate. After removal of the solvent from the ether solution, the remaining oil was distilled. The half ester was collected at 165–170° (10 mm.) as colorless viscous oil. Saponified with alkali, *cis*-caronic acid was obtained.

From Isoamyl Hydrogen *cis*-Caronate to *trans*-Caronic Acid.—Five grams of the half ester above described was added to 20 cc. of petroleum ether and next 3 g. of thionyl chloride was added drop by drop under cooling with ice and was left stand over night. Then it was warmed on a water-bath for half an hour. The petroleum ether and excess of thionyl chloride were removed under reduced pressure on a water-bath and crude isoamyl ester chloride of *cis*-acid was obtained. This was heated at 200° on an oil-bath for three hours. After cooling, water was added and, boiled for three hours and the reaction mixture was saponified. Then it was extracted with ether. The ether solution was dried on anhydrous sodium sulfate. After removal of the solvent from the ether solution the remaining oil was distilled under reduced pressure and the distillate, which boiled untill the temperature of the bath rose to 220° at 10 mm., was discarded. The remainder crystallized on cooling. It was recrystallized from water and showed m.p. 212°. The test of the melting point, when mixed with *trans*-caronic acid, did not cause the depression of the melting point.

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