

hooks a, in order to hold the two parts tightly and the tube B is connected with the carbon dioxide generator. The rest of the procedure is as described by Pregl.

2. In this one-piece Pregl's apparatus (Fig. 2) the carbon dioxide is led into the decomposition flask A through the tube D drawn into a capillary and entering the side arm B of the flask. This tube fits tightly at the outer end of the side arm by means of a ground-glass joint C. After the apparatus has been charged through the side arm B, the inside of the latter and the ground joint C are moistened with hydriodic acid and the tube D inserted. Then the rubber tube leading to the carbon dioxide generator is slipped over the end of the glass tube D and over the ground-glass joint. There is no retention of alkyl iodide in the side arm on account of the presence of hydriodic acid.

Numerous methoxyl determinations with either modification 1 or 2 have demonstrated that boiling is smooth, bumping does not occur, accurate results are obtained and almost no attention to the operation is necessary after the initial adjustment of the carbon dioxide stream and the microburner.

CONTRIBUTION FROM THE
LABORATORIES OF THE
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D. RIGAS RIGAKOS

COMMUNICATIONS TO THE EDITOR

THE STRUCTURE OF THE FERROCYANIDES

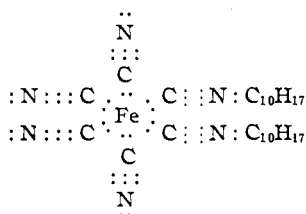
Sir:

A recent contribution by Stephen and Hammerich [*J. prakt. Chem.*, **129**, 285-308 (1931)] on the action of ferrocyanic acid on bicyclic terpenes leads to some interesting conclusions with regard to the structure of the addition compounds.

These investigators have studied the addition of ferrocyanic acid to such compounds as camphene, α -pinene and nopinene, getting compounds corresponding to the formula $(C_{10}H_{17})_2H_2Fe(CN)_6$. Most of the product rearranges on treatment with alkalis but there is a 7% yield of an amine and an alcohol called by the authors isobornylamine and isoborneol. The presence of these two products seems to call for the existence of two forms of the addition product—one completely ionized and the other only partially so.

To obtain isoborneol from the hydrolysis of the α -pinene addition product we may assume complete ionization of the compound $(C_{10}H_{17})_2H_2Fe(CN)_6$, the hydroxyl from water attaching itself to the cation $C_{10}H_{17}$. Potassium formate, ammonia and ferrous hydroxide are the other products.

To obtain isobornylamine, however, we are led to the conclusion that there is some sort of connection between the nitrogen and the $C_{10}H_{17}$ group probably as follows



Tetra-covalent nitrogen is not unique; nevertheless, the experimental evidence presented by these investigators leads to conclusions which may be interesting as applied to the structure of the complex ferrocyanides.

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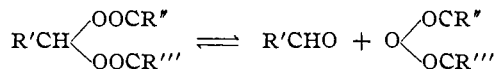
HOWARD W. POST

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A NEW SERIES OF HOMOGENEOUS MONOMOLECULAR GAS REACTIONS

Sir:

In the course of a systematic investigation of equilibria and reaction velocities in gaseous and liquid "ester-acid anhydride-aldehyde" systems from points of view outlined elsewhere [Coffin and Maas, *Canadian Journal of Research*, **3**, 526 (1930); **3**, 540 (1930)], a new series of homogeneous monomolecular reactions has been found. Several examples of the gaseous decomposition represented by the general equation



have been found to be monomolecular in accordance with modern ideas regarding the break-up of complicated molecules. In the cases already investigated the reaction is homogeneous and follows the Arrhenius equation. The heats of activation and the absolute temperatures at which the reactions attain a given rate fall in well with the parallelism displayed by known examples of monomolecular change. Experiments are being carried out at present to determine whether or not the rate constant falls off as the pressure is lowered.

As the reaction appears to be particularly well adapted for an investigation of the influence of molecular structure on reaction velocity, the decomposition of as many as possible homologous and isomeric esters is being studied. A description of the experimental method together with the results obtained to date will be published shortly.

It is of interest in connection with the "dreierstoss" theory that in none