CONTROLLED FORMATION OF *cis*- AND *trans*-DECALIN-9-CARBOXYLIC ACIDS BY CARBONYLATION

Sir:

Koch and Haaf[1] have described the preparation of decalin-9-carboxylic acid (80% *cis*) from β-decalol, sulfuric and formic acids. In a recent use of this preparation, we have found that products all the way from 84% *cis* (V) to 90% *trans* (IV) can be obtained, the only variable being the amount of fuming sulfuric acid included in the reaction medium (see Table I).

TABLE I

COMPOSITION OF DECALIN-9-CARBOXYLIC ACID IN PREPARATIONS BY UNIFORM PROCEDURE

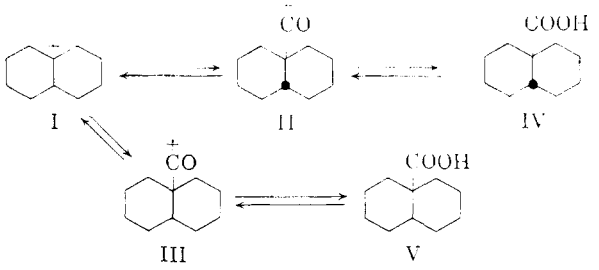
41.5 g. 98% H_2SO_4; 4.6 g. 88% formic acid; 0–5°, 1–1.5 hr.

30% oleum, g.	% *trans* (10.29 μ)	% *cis* (11.26 μ)	100-(% *cis*) − (% *trans*)
None	90	10	0
5	74	22.5	3.5
10	56	41	3
15	19	62.5	18.5
20	5	84	11
40	7.5	79	13.5
(Isomerization product)	9	87.5	3.5

For the rapid assay of the total acid fraction calibration curves were prepared by the infrared examination of six synthetic mixtures of the purified isomers (*cis*, m.p. 122°; *trans*, m.p. 135°) at total concentrations of 25 mg. of acid per cc. of carbon disulfide. Estimates made separately from the "*trans*" peak at 10.29 μ and the "*cis*" peak at 11.26 μ agreed within 3% on isomer composition of the products made with 0–10 g. of fuming sulfuric acid present, but indicated the presence of 11–18% of a further isomer from the more strongly acid media.

A sample of the acid assaying 90% *trans* was introduced into a mixture of 41.5 g. of 98% sulfuric acid and 20 g. of fuming sulfuric acid (30%), along with 5 g. of formic acid, over a period of 10 minutes. After 1.5 hours at 5° decalin-9-carboxylic acid was recovered in 90% yield, having the composition 87.5 *cis*, 9% *trans*. Thus kinetic control of carbonylation leads to *trans*-decalin-9-carboxylic acid, eventual equilibrium favoring the *cis* isomer.

Models show that the *trans*-acylium ion II,



with the C—C≡O⁺ atoms in a straight line, has little axial-axial interaction and should be rapidly formed without strain. On the other hand, in the *trans* acid IV, or its protonation product, the axial carboxyl appears more crowded than a methyl group, which in analogous cases is known to reverse the usual order of stability and to favor the *cis*-decalin system over the *trans*.[2,3,4,5]

In strong enough acid to make all the steps reversible, equilibrium is approached; K = (V)/(IV) = 4–11 at 5°, depending upon the composition of the unisolated 10% of the material. This is consistent with the value 1.5 at 250° obtained for 9-methyl-1-decalone.[3]

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DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASS.

RICHARD E. PINCOCK
ERNST GRIGAT
PAUL D. BARTLETT

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ON THE MECHANISM OF THE ENZYMATIC DECARBOXYLATION OF ACETOACETATE[1]

Sir:

In order to investigate the mechanism of the enzymatic decarboxylation of β-ketoacids, we have examined the oxygen exchange which accompanies the decarboxylation of acetoacetic acid, labeled in the carbonyl group with O^{18}, in the presence of the crystalline[2] decarboxylase from *Clostridium acetobutylicum*.

Acetone was labeled with O^{18} by allowing it to stand with enriched water (Stuart Oxygen Co., 1.4% O^{18}) and a trace of sodium hydroxide. Ethyl acetoacetate was saponified in 2 *M* potassium hydroxide in enriched water, and the potassium acetoacetate, labeled in the carbonyl and carboxyl groups, was obtained by evaporation *in vacuo* and purified by precipitation of an alcoholic solution with ether. The O^{18} content of the acetone was determined mass spectrometrically by measuring the ratio of the 58 and 60 peaks, using a Consolidated model 21-103C mass spectrometer; the cracking pattern of the acetone established its purity. Acetone from the enzymatic decarboxylation and from control experiments was swept from the reaction mixture with a stream of air through an ice-water condenser, and trapped at −78°. A sample of acetone vapor then was prepared for mass spectrometry by equilibrating liquid and vapor at 0°. Some water undoubtedly was present in the liquid sample, but earlier work[3] has shown that, in the absence of buffers, exchange between acetone and water at low temperatures is very slow. The internal consistency of the results further supports this conclusion. Control experiments with potassium acetoacetate were conducted by freezing the solution after 2.5

(1) This research was supported in part by a grant from the National Institutes of Health.

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