point with an authentic 2-chloropyridine picrate gave no depression.

Anal. Calcd. for $C_{11}H_7N_4O_7Cl$: N, 16.36. Found: N, 16.53.

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The Biosynthesis of Valine in *Aerobacter Aerogenes*[1]

BY MAX E. RAFELSON, JR.

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Strassman, *et al.*,[2] have shown by isotopic studies in *Torulopsis utilis* that pyruvic acid was apparently the sole source of the carbon chain of valine. The distribution of the carbon atoms of glycine and acetate as well as carbon 1 of glucose was in accord with their prior conversion to pyruvate *via* known biochemical processes.

As a result of experiments designed to study the biosynthesis of tryptophan,[3,4] various radioactive valine samples were isolated from *Aerobacter aerogenes* grown on acetate-1-C^{14}, glucose-1-C^{14} and glucose-3,4-C^{14}. These valine samples were subjected to degradation in order to determine the intramolecular distribution of the isotope. The results are presented in Table I and are identical with those obtained by Strassman, *et al.*,[2] in *T. utilis*. This may be interpreted as indicating that the biosynthetic pathways for valine in these two organisms are very similar, if not identical. The present data are in accord with the proposed mechanism for valine biosynthesis.[2] This visualized the prior conversion of glucose and acetate to pyruvate and the subsequent condensation of pyruvate and acetaldehyde (derived from pyruvate by decarboxylation) to yield α-acetolactate which undergoes a pinacol-like rearrangement to form the keto analog of valine.

TABLE I

INTRAMOLECULAR DISTRIBUTION OF GLUCOSE AND ACETATE CARBON IN VALINE

Valine carbon atom	Total activity in valine, % Glucose C-1	Glucose C-3,4	Acetate C-1
1	2	100	99
2	4	0	0
3	4	0	0
4,4[1]	90	0	0

Experimental

The cultivations of the organism on acetate-1-C^{14} and on glucose-3,4-C^{14} have been described in previous publications.[3,4] The details of the glucose-1-C^{14} cultivation[5] were very similar to those of the cultivation on glucose-3,4-C^{14}. The procedures for the assay of radioactivity have also been presented in detail.[3,4,6]

Following the removal of tryptophan, tyrosine and phenylalanine from the hydrolysates,[3,6] glutamic and aspartic acids were separated from the hydrolysate according to Cannan.[7] The remaining amino acids were separated on a column of Dowex-50.[8] The fractions containing valine were treated as described by Ehrensvärd, *et al.*[9] The identity and purity of the valine samples were determined by filter paper chromatography and radioautography.

The methods for the degradation of valine were essentially those of Strassman, *et al.*,[2] the differences being minor.

(1) Supported in part by a grant (G-4175) from the National Institutes of Health, United States Public Health Service.

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Steric Effects on Migration Aptitudes. Reaction of Some *o*-Substituted Benzophenones with Peroxyacetic Acid

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It has been known for some time that the migration aptitude of a *p*-substituted phenyl group in the pinacol and allied rearrangements depends upon the electron-releasing ability of the substituent. The abnormally low migration aptitudes of *o*-substituted phenyl groups have been explained on the basis of a steric effect,[1] and recently the nature of this steric effect has been discussed in some detail.[2] According to this viewpoint the migrating aryl group must adopt a rotational conformation such that the π-electrons of the ring may effectively overlap the vacant (or partially vacant) *p*-orbital left by the departing group on the migration terminus. An *o*-substituent interferes with this process and thus lowers the mobility of the group.

The data on the pinacol rearrangement give no indication as to whether the major source of interference with the *o*-substituent lies in other groups on the migration origin or in groups on the migration terminus. An answer to this question would be of considerable assistance in formulating a more precise picture of the transition state for the rearrangement. One possible approach is the selection of a system in which there are no interfering substituents on the migration terminus. Kharasch[3] found that in the treatment of tertiary aromatic alcohols with hydrogen peroxide under acidic conditions, which leads to phenols and ketones, both *o*-anisyl and *o*-tolyl migrated better than phenyl, in contrast to behavior of these groups in the pinacol rearrangement. Here there is no possibility of interference by groups on the migration terminus, since the only such group in the protonated hydroperoxide intermediate is the departing $-OH_2^+$, which must be *trans* to the migrating group. Unfortunately there was not a sufficient variety of substituents employed to permit a decision concerning the degree of similarity between this reaction and the pinacol rearrangement. Another recent study of the *ortho* effect, in which Smith[4] deter-

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