

occurred between allyl bromide and  $\gamma$ -tocopherol in the absence of the zinc chloride catalyst.

### Summary

The formation of a coumaran derivative on

treatment with allyl bromide and the formation of dimethylmaleic anhydride on oxidation indicate that  $\gamma$ -tocopherol is 7,8-dimethyltolcol.

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## NOTES

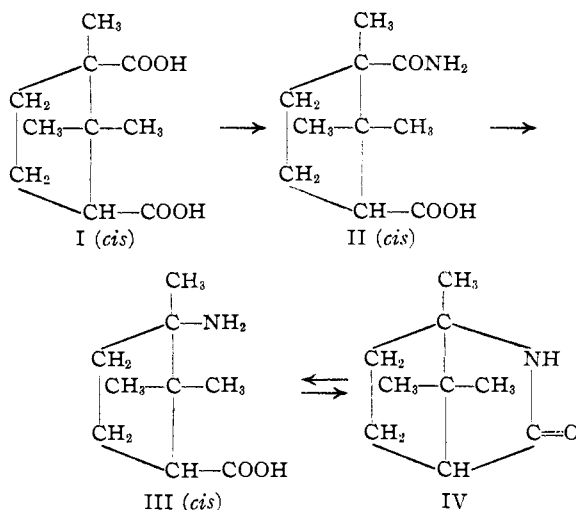
### The Walden Inversion and the Hofmann Rearrangement

BY S. ARCHER

For many years it has been merely assumed that the carbon atom that migrates to the nitrogen atom in the Hofmann rearrangement retains its configuration during the change.<sup>1</sup> Recently Bartlett and Knox<sup>2</sup> demonstrated that this reaction could proceed without inversion. However, the type of compounds used did not permit any unqualified statement concerning the stereochemistry of the migration. These authors state that "... no inversion or series of inversions, need be involved in the Hofmann rearrangement." It therefore seems proper to point out that there has long existed in the literature experimental evidence to prove that no inversion of configuration occurs in the Hofmann reaction. This evidence is in the papers of W. A. Noyes and his co-workers.<sup>3</sup>

Camphoric acid (I) was converted to  $\beta$ -camphoramidic acid (II) (*cis*). Treatment with hypobromite gave aminodihydrocampholytic acid (III), which, when heated for ten minutes with a solution of sodium acetate in acetic anhydride, gave the lactam (IV). The latter upon hydrolysis gave the amino acid (III) in optically pure form,

showing that no inversion took place during lactamization. The amino and carboxyl groups in (III) must therefore be *cis* to each other. Since the starting acid (I) was of the *cis* series and since the only reaction wherein inversion might have occurred was the Hofmann rearrangement, it must be concluded that no inversion took place



when the amide (II) was converted to the amine (III). If, on the other hand, inversion had occurred during the conversion of II to III, the latter would have been of the *trans* series, which is contrary to fact.

The same set of reactions was carried out on the three isomers of  $\beta$ -camphoramidic acid. Substantially the same result was obtained in each case, namely, that no inversion took place during the Hofmann rearrangement.

(1) (a) Braun and Friehmelt, *Ber.*, **66**, 684 (1933); (b) Arcus and Kenyon, *J. Chem. Soc.*, 916 (1939); (c) Bernstein and Whitmore, *This Journal*, **61**, 1324 (1939).

(2) Bartlett and Knox, *ibid.*, **61**, 3184 (1939).

(3) (a) Noyes, *Am. Chem. J.*, **16**, 500 (1894); (b) Noyes and Potter, *This Journal*, **37**, 189 (1915); (c) *ibid.*, **34**, 1067 (1912); (d) Noyes and Nickell, *ibid.*, **36**, 118 (1914). These papers give an account of the conversion of a half-amide of camphoric acid or isocamphoric acid to an amino acid by the Hofmann reaction. There was no optical inversion in any of the reactions. In the paper by Potter and myself, *ibid.*, **34**, 1068 (1912), however, a Walden inversion and structural rearrangement caused by nitrous acid is described. The Hofmann reaction was not involved in this.—W. A. Noyes.

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