We have previously suggested[2] that the formation of a sulfenic acid can be considered a reversible thermal six-electron sigmatropic rearrangement. This is allowable as the hydrogen atom involved in transfer from the methyl group to the sulfoxide oxygen has a symmetrical electron distribution (s orbital). Thus effective orbital overlap can be established between the oxygen p orbitals and the hydrogen atom in the forward sense, and the carbon–carbon double-bond π orbitals and the hydrogen atom in the reverse sense.

The deuteration is remarkably stereospecific. As a consequence of the sigmatropic rearrangement, the readdition of the sulfenic acid to the olefin gives of necessity deuterium in the methyl group cis to the sulfoxide. The configuration of the products can be controlled by two possible factors. The first, which we prefer, is the thermodynamic stability of the product, since in all cases the recovered sulfoxides have the same stereochemistry as the starting sulfoxides, which we have previously shown[7,8] to be resistant to isomerization. An alternative viewpoint would concern the intermediate sulfenic acid which due to hydrogen bonding to the NH in the amido side chain has a restricted conformation. Ring closure would then occur on the β face of the molecule, except in the case of no NH in the side chain (phthalimido) when steric effects would operate[10] and ring closure occur on the α side.

In qualitative terms, temperature requirements for deuterium incorporation are less, and the degree of incorporation more, for **1b** than for **1a**. This could be from one or both of two effects:[11] either the presence of hydrogen bonding in **1a** would decrease the electron density of the sulfoxide oxygen and thereby decrease the effective orbital overlap with the hydrogen of the methyl group; or alternatively, the greater electron-withdrawing power of the phthalimido group weakens the sulfur–carbon bond and lowers the activation energy of the process.[12]

Acknowledgments. I wish to acknowledge valuable discussions with Dr. L. D. Hatfield and Dr. B. B. Molloy of these laboratories and Dr. J. E. Baldwin of Massachusetts Institute of Technology.

(10) Steric control was previously suggested[9] as the reason for the formation of the α-sulfoxide from the oxidation of phthalimidopenicillin.

(11) A referee has suggested the possible alternate explanation that the rate difference is due to the higher ground-state energy of the phthalimido derivative because of considerable steric interaction of the β-methyl group with a carbonyl function of the phthalimido group.

(12) Experiments with a suitably substituted series of side chains are in progress to test this hypothesis and to obtain a value for the activation energy.

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Book Reviews

The Chemistry of the Isoquinoline Alkaloids. By TETSUJI KAMETANI, Tohoku University, Aobayama, Sendai, Japan. Hirokawa Publishing Co., Inc., 27-14 Hongo 3-chome, Bunkyo-ku, Tokyo. 1968. 265 pp. 18 × 26 cm. $18.90.

The number of recorded isoquinoline alkaloids, already impressively large, is constantly expanding because of the availability of vastly improved methods of isolation and characterization. Consequently, the task of establishing the novelty of newly discovered alkaloids can assume heroic proportions. Under these circumstances the greatest boon to those interested in the field is access to a reliable and systematic description of what is already known. This is precisely what Professor Kametani has provided in his new book (also to be made available soon by American Elsevier Publishing Co.), which is a compilation of an enormous amount of informative data, readily accessible and attractively printed. The first chapter is an introduction which is a masterful condensation of background material covering structural determination, chemical synthesis, biogenesis, and biosynthesis of the isoquinoline alkaloids. This is followed by 23 chapters of concisely presented data for the alkaloids which are grouped according to structure and/or biogenesis. The data in the text are complete through 1966 and are updated through 1967 with an appendix.

Unfortunately, no undertaking of this scope can be completely free of errors and oversights. Examination of Chapter 17, "Emetine and Related Alkaloids," pp 160–166, reveals the following. (1) Representation of the sterochemistry at C-1′ is not consistent—it is given for tubulosine and some other alkaloids and omitted for cephaeline and others. (2) Almarckine does *not* occur in *A. lamarckii* as indicated. (3) The empirical formula for emetine is $C_{29}\ldots$, *not* $C_{20}\ldots$. (4) Reference 119 is incomplete—two authors are omitted. A more serious criticism is the deviation from the stated organization of the book, namely, "The compounds are arranged with respect to their molecular weight." Unfortunately this arrangement, the value of which is enhanced by the wide application of mass spectra, is not always followed (see pp 90, 131, 162, and 163 as random examples).

Despite these critiques, Professor Kametani's contribution is monumental. Everyone working with isoquinoline alkaloids owes him a debt of gratitude for this monograph which is a valuable addition to the existing library on alkaloids. It is this reviewer's fervent wish that Professor Kametani will augment its usefulness by frequent and regular updating.

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