on Magnesol–Celite under such developmental conditions that monosaccharide derivatives were removed from the column. β-D-Glucose pentaacetate was identified in the effluent and β-D-maltose octaacetate in the bottom zone (identifications by melting point, mixed melting point and rotation). The next higher zone was twice rechromatographed in the same manner and the eluent which crystallized from ethanol was identified as β-D-isomaltose octaacetate (m. p. 144–145°, unchanged on admixture with an authentic specimen; $[\alpha]^{25}\text{D} +96°$, c 2.0, chloroform); yield 50 mg.

Repetition of the previously described procedure[4] with the substitution of corn amylose for animal glycogen, failed to yield any β-D-isomaltose octaacetate by chromatography.

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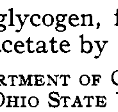
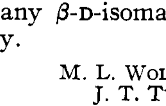
THE SYNTHESIS OF PATULIN

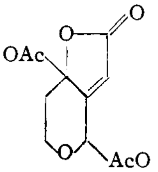
Sir:

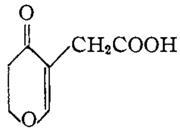
We have reported elsewhere[1,2] the considerations which led us to propose the structure (I, R = H) for patulin. The evidence now available[1,2,3,4] in favor of that expression may be regarded as conclusive. A partial synthesis of the antibiotic has already been achieved.[4] We now wish to record the total synthesis of patulin.


I


II

The lactol acetate (II)[1] in carbon tetrachloride in the presence of a trace of benzoyl peroxide rapidly consumed one mole of N-bromosuccinimide. When the crude bromination product was taken up in acetic acid and treated with silver acetate, the diacetate (III) m. p. 142–143° (Calcd. for $C_{11}H_{12}O_7$: C, 51.56; H, 4.69. Found: C, 51.91; H, 4.80), was formed. The structure of the diacetate was confirmed through its conversion, by hydrogenation over reduced platinum oxide in pure dioxane followed by hydrolysis with warm hydrochloric acid, to **desoxypatulinic acid (IV)**.[4]


III


IV

Treatment of the pure diacetate (III) for a short time with warm acetic anhydride–acetic acid–sulfuric acid[1] gave a complex mixture of substances from which patulin acetate (I, R = Ac) was readily isolated in 1–2% yield by taking advantage of the fact that in ethereal solution it traveled more rapidly through a column of Brockmann alumina than its congeners. The pure synthetic acetate melted at 114–116°, alone or in admixture with the acetate (m. p. 115–116.5°) from natural patulin. The ultraviolet ($\lambda_{\max.}$ 277 mμ) and infrared spectra of the synthetic and natural samples were identical. The ready hydrolysis of patulin acetate to patulin is well known.[5]

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[1] Woodward and Singh, THIS JOURNAL, **71**, 758 (1949).

[2] Woodward and Singh, *Experientia*, in press.

[3] Dauben and Weisenborn, THIS JOURNAL, **71**, 3853 (1949).

[4] Woodward and Singh, *Nature*, in press.

[5] *Cf.* Bergel, Morrison, Moss and Rinderknecht, *J. Chem. Soc.*, 418 (1944).

ON THE MECHANISM OF OXIDATION OF INDOLE COMPOUNDS[1,2]

Sir:

Perbenzoic acid cleaves indole compounds[3] in the same way as ozone,[4] or, in some cases, peracetic acid.[5] It was possible to isolate as an intermediate in these reactions derivatives of β-hydroxyindolenines in the case of some natural products in which internal addition to the reactive C=N bond blocked further oxidation.[6]

In accordance with this view 11-hydroxytetrahydrocarbazolenine (I)[7] reacted smoothly with perbenzoic acid to yield the 9-membered cyclic lactam II (magnificent, slightly yellow prisms from ethyl acetate, m. p. 157°. *Anal.* Calcd. for $C_{12}H_{13}O_2N$: C, 70.94; H, 6.40; N, 6.9. Found: C, 71.05; H, 6.76; N, 6.8). II was also obtained from 11-hydroperoxytetrahydrocarbazolenine[8] (III) by a rearrangement that was almost quantitative under neutral or slightly acidic conditions. The change in the latter case seems to be analogous to some peroxide rearrangements involving intermediate cationoid oxygen.[9,10] The kinetic evaluation of this interesting rearrangement is in progress. Under the action of cold 2 *N* aqueous alkali on II, the initially yellow solution (salt of the enol of II) became slightly warm and then decolorized.

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[1] This investigation was supported by a grant-in-aid from Research Corporation, New York.

[2] Directed Oxidations in the Indole Series. IV.

[3] Witkop and Fiedler, *Ann.*, **558**, 91 (1947).

[4] Witkop, *ibid.*, **556**, 103 (1944).

[5] Witkop, *ibid.*, **558**, 98 (1947).

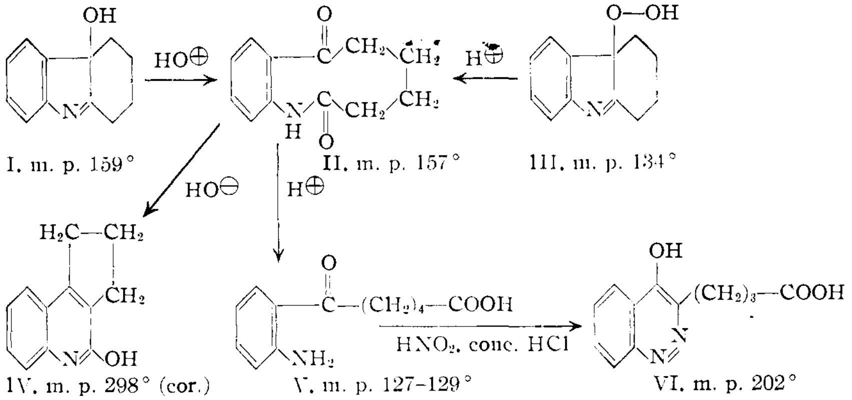
[6] Witkop, in preparation.

[7] Patrick and Witkop, THIS JOURNAL, **72**, 633 (1950).

[8] *Cf.* Beer, McGrath, Robertson and Woodier, *Nature*, **164**, 362 (1949).

[9] Criegee, *Ann.*, **560**, 127 (1948).

[10] Leffler, *Chem. Reviews*, **45**, 385 (1949).



I. m. p. 159°; II. m. p. 157°; III. m. p. 134°; IV. m. p. 298° (cor.); V. m. p. 127–129°; VI. m. p. 202°

This corresponds to the conversion of II, by loss of water, into IV (colorless rods from water, m. p. 298°, blackening. *Anal.* Calcd. for $C_{12}H_{11}ON$: C, 77.88; H, 5.96; N, 7.56. Found: C, 77.73; H, 6.17; N, 7.57 (burned with copper oxide)). IV, by analogy, would be expected to have the structure of 4-keto-2,3,4,5-tetrahydro-α-quinindene,[11,12] rather than the alternative linear formulation.[13,14] Mild acid hydrolysis of II gave V exhibiting all the properties of the known δ-*o*-aminobenzoylvaleric acid[15] (slightly yellow prisms from alcohol, m. p. 129°. *Anal.* Calcd. for $C_{12}H_{15}O_3N$: C, 65.15; H, 6.79; N, 6.33. Found: C, 64.85; H, 6.89; N, 6.18). V with nitrous acid in concentrated hydrochloric acid formed the cinnoline (VI) recently described.[16]

The significance of the model reactions reported here will be demonstrated shortly.

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[11] *Cf.* The Ring Index, New York, 1940, Structure No. 1764.

[12] The melting point of IV is 42° higher than is reported for 4-keto-2,3,4,5-tetrahydro-α-quinindene (256°) [Blount, Perkin and Plant, *J. Chem. Soc.*, 1975 (1929)]. The isomeric 9-keto-2,3,4,9-tetrahydro-β-quinidene is reported to melt at 327°. The synthesis of these compounds for comparison with (IV) is in progress.

[13] *Cf.* Camps, *Ber.*, **32**, 3228 (1899); *Arch. d. Pharm.*, **237**, 659 (1899).

[14] *Cf.* Huisgen, *Ann.*, **559**, 101 (1947).

[15] Perkin and Plant, *J. Chem. Soc.*, **123**, 676 (1923).

[16] Keneford and Simpson, *ibid.*, 2318 (1948).

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NEW BOOKS

Electronic Interpretations of Organic Chemistry. By A. EDWARD REMICK, Ph.D., Associate Professor of Chemistry, Wayne University, Detroit. Second Edition. Chapman and Hall, Limited, London. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1949. vii + 600 pp. Illustrated. 15.5 × 23.5. Price, $6.00.

A book describing modern organic chemical theory is dated in a very short time. It is therefore gratifying that this book which first appeared in 1943 has been extensively revised and brought up to date. In the process of revision the book has been expanded by over a hundred pages in spite of the fact that the appendices on physico-chemical background material were left out and the historical introduction was abridged. The chapter on chemical physics has been almost completely rewritten, and while the applications of the older (pre-1935) electronic theories have been cut down, most of the topics appear in later sections as applications of present theoretical concepts. Many new studies in reaction mechanisms are included. An excellent chapter on contributions from the field of stereochemistry appears for the first time.

The author usually treats the "English" theories and "American" quantum mechanical and resonance concepts separately, a stratagem which may be necessary because the two schools use different though parallel terminology. The reviewer feels, however, that much more correlation between the two approaches could have been accomplished to make clear their essential similarity.

The main criticism must be levelled at the discussion of resonance. Firstly, no matter how much explanation is given, to say that the molecule *resonates*, leaves an impression in the reader's mind that the molecule *does* something, that there are electronic movements between extreme positions. The pendulum analogy is unfortunate, since the two pendulums exist even when uncoupled, while the contributing resonance structures have only imaginary existence (pp. 110–111). The discussion of the actual nature of a molecule exhibiting resonance is confused (p. 109). According to Bridgman's operational approach (also implied in Wheland's views), it is meaningless to discuss whether the electrons oscillate, are stationary, or are "smeared out," when no conceivable physical measurement can distinguish between the alternatives. The inductive and mesomeric "electron displacements" are also imaginary movements of electrons since the initial configurations (the normal valence bond structures) do not occur in nature. Only the inductomeric and electromeric displacements are postulated as actual electronic movements. In this connection it is misleading to use the expression "*Moment* of reaction" (p. 54).

The postulates collected at the end of the book are useful for reference purposes but require much interpretation before being of use in predicting reactions. For instance, it is difficult to understand postulate (P) 7: "The electromeric effect, except when unusually weak, is much more powerful than any of the other electron displacements." In postulates 16–20 it is not always clear what "Other things being equal" means. Thus two contributing resonance structures with differing numbers of covalent bonds (P 16) also have differing charge distributions or a different number of unshared electrons.

A few errors and omissions were noted. The Berliners in their work on hyperconjugation (p. 134), far from dis-