measured on a Hilger-Watts diffractometer using Ni-filtered Cu Kα radiation. The reflection data were corrected for absorption [μ = 42.7 cm^{-1}]. Of the 1177 independent reflections for $\theta < 57°$, 1086 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was resolved by Patterson and Fourier methods and was refined by full-matrix least squares to $R = 0.036$ and $wR = 0.044$ (nonhydrogen atoms anisotropic, hydrogen atoms isotropic and not refined).

The absolute configuration was determined by carrying out two refinements, one using the correct value of the imaginary part of the anomalous dispersion corrected for bromine ($\Delta f''$) and the other with the sign of $\Delta f''$ reversed (equivalent to refining the antipode). The weighted discrepancy indices at the end of the two refinements were 0.0436 and 0.0540 for $\Delta f''$ and $-\Delta f''$, respectively. Thus, according to the test described by Hamilton,[23] the absolute configuration is established at better than the 0.995 confidence level.

Acknowledgment. The authors wish to thank Dr. E. P. Oliveto for his interest and stimulating discussions of this work. We also with to thank Drs. W. Benz, V. Toome, and T. Williams and Mr. S. Traiman for mass, UV, NMR, and IR spectra, respectively, as well as Dr. F. Scheidl for the microanalyses.

Registry No. (±)-1, 64911-60-0; (+)-1, 52775-76-5; (±)-2, 71749-31-0; (±)-3, 71749-32-1; (±)-4, 71749-33-2; (±)-5, 71749-34-3; (+)-5, 71773-00-7; (−)-5 (*R*)-(+)-α-methyl-*p*-nitrobenzylamine salt, 71773-02-9; (+)-5 (*S*)-(−)-α-methyl-*p*-nitrobenzylamine salt, 71806-47-8; (±)-6, 71749-35-4; (+)-6, 71773-03-0; 7, 71749-36-5.

Supplementary Material Available: Experimental Section providing preparation details for the compounds in the text (6 pages). Ordering information is given on any current masthead page.

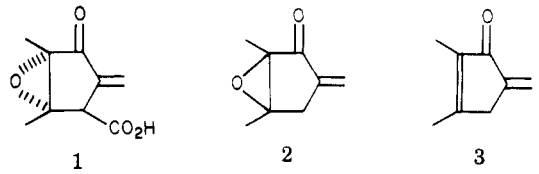
(23) W. C. Hamilton, *Acta Crystallogr.*, 18, 506 (1960).

Jane Jernow,* William Tautz, Perry Rosen John F. Blount
Chemical Research Department
Hoffmann-La Roche Inc.
Nutley, New Jersey 07110
Received June 26, 1979

Methylenomycin B: Revised Structure and Total Syntheses

Summary: Starting from 2,3-dimethylcyclopent-2-en-1-one (4), it has been shown that methylenomycin B is not the epoxide 2 as reported, but rather 2,3-dimethyl-5-methylenecyclopent-2-en-1-one (3).

Sir: In the previous communication, we describe the total synthesis of methylenomycin A (1).[1] The related antibiotic methylenomycin B was isolated as an unstable oil, and on the basis of spectral evidence[2] was assigned structure 2. However, analysis of these spectral data did not lend support to the assigned structure,[3] and indeed led us to propose compound 3 as the material isolated as methylenomycin B. To confirm this, both compounds 2 and 3 were synthesized.



1 2 3

Starting with ketone 4 (prepared from methylmagnesium iodide and the *N*-pyrrolidine enamine of 3-methyl-1,2-cyclopentanedione),[4] alkaline hydrogen peroxide treatment produced epoxide 5 [47%,[5] bp 80–81 °C (20 mm)] (Scheme I). The introduction of the α-methylene function was carried out via the hydroxymethyl compound 6, which was prepared by the procedure of Grieco and Hiroi[6] (50%, LDA and gaseous CH_2O). An analytical sample of 6, purified via chromatography, appeared to be homogeneous: IR ($CHCl_3$) 3630, 3550 (br), 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.36 (s, CH_3), 1.51 (s, CH_3) 1.83, 2.28[7] (2 dd, J = 7, 3 Hz, ring CH_2), 2.45 (m, CH, OH), 3.75 (m, CH_2O–); MS m/e 156 (M^+); GC–MS (Me_3Si derivative) m/e 228 (M^+). For the total synthesis of 2, crude 6 was subjected to dehydration (DCC, CuCl). After column chromatography on neutral silica gel followed by distillation [molecular, bath temperature 35 °C (0.2 mm)], compound 2 was isolated in an overall yield of 15% from 5:[8] IR (neat) 1735, 1650 cm^{-1}; UV λ_{max} (CH_3OH) 228–229 nm (ε 7050); ^{1}H NMR ($CDCl_3$) δ 1.45 (s, CH_3), 1.54 (s, CH_3), 2.75 (tq, ring CH_2, J = 2.5 and 18 Hz), 5.39, 6.13 (2 t, CH_2=, J = 2.5 Hz); MS m/e 138 (M^+). Although these data are in agreement with structure 2, they are distinct from those published for methylenomycin B[2]. This confirmed our earlier suspicion of the erroneous structure assignment.

The preparation of 3, our proposed alternate structure for methylenomycin B, started with enone 4 (Scheme II). It was transformed as described previously for compound 6 into compound 7 [bp 80–82 °C (0.2 mm)] in 53% yield: IR ($CHCl_3$) 1675, 1635 cm^{-1}; UV λ_{max} (CH_3OH) 236 nm (ε 12720); ^{1}H NMR ($CDCl_3$) δ 1.69 (s, CH_3), 2.06 (s, CH_3), 2.3–2.9 (m, ring CH_2CH), 2.99 (br s, OH), 3.80 (m, CH_2O); MS m/e 140 (M^+). The structure of 7 was confirmed by an X-ray analysis of its *p*-bromobenzoate ester (mp 91–93 °C). Compound 7 was smoothly transformed (DCC, CuCl) into 3, which after distillation [molecular, bath temperature 37 °C (0.3 mm)] was obtained in 80% yield: IR (neat) 1690, 1662, 1630 cm^{-1}; UV λ_{max} (CH_3OH) 242 (ε 10000); 260–266 nm (sh, ε 7900); ^{1}H NMR ($CDCl_3$) δ 1.78 (br s, CH_3), 2.07 (br s, CH_3), 3.08 (br s, ring CH_2), 5.34, 6.04 (2 t, CH_2=); MS m/e 122 (M^+). A comparison of the IR, UV,

(1) J. Jernow, W. Tautz, P. Rosen, and J. F. Blount, *J. Org. Chem.*, preceding paper in this issue.
(2) T. Haneishi, N. Kitahara, Y. Takiguchi, M. Arai, and S. Sugawara, *J. Antibiot.*, 27, 386 (1974); T. Haneishi, A. Terahara, M. Arai, T. Hata, and C. Tamura, *ibid.*, 27, 393 (1974).
(3) Despite the fact that methylenomycin B was reported to have a microanalysis of $C_8H_{10}O_2$, with m/e 138 (M^+) and a zero optical rotation.
(4) According to the method of Dahill for the preparation of 2-*n*-amyl-3-methylcyclopent-2-en-1-one: R. T. Dahill, Jr., *J. Org. Chem.*, 31, 2694 (1966).
(5) Because of the alkali sensitivity of 5, this reaction has to be terminated when the rate of destruction overtook the production of 5.
(6) P. A. Grieco and K. Hiroi, *J. Chem. Soc., Chem. Commun.*, 1317 (1972).
(7) In a cyclopentane system, an epoxide deshields the cis vicinal proton. The C(4) proton which absorbs at δ 2.28 (downfield) is therefore cis to the epoxide. It must be, at the same time, trans to the C(5)-H as deduced from the small J = 3 Hz, and in contrast to J = 7 Hz for the C(4) proton, which absorbs at δ 1.83, indicating cis relationship to the C(5)-H. Therefore, the hydroxymethyl group at C(5) must be cis to the epoxide in the analytical sample of 6.
(8) All yields were based on analytical samples purified by distillation, crystallization, or sublimation.

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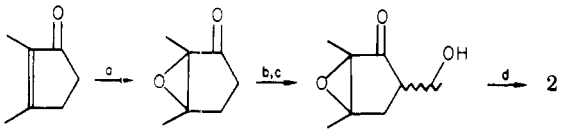
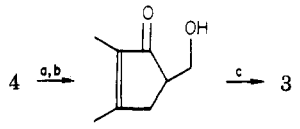
Scheme I



(a) 30% H_2O_2, Na_2CO_3; (b) LDA; (c) CH_2O; (d) DCC, CuCl.

Scheme II

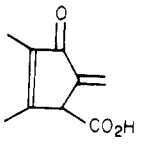


(a) LDA; (b) CH_2O; (c) DCC/CuCl.

and NMR spectra with those previously reported[2] clearly showed that the structure of the material isolated as methylenomycin B should be reassigned as **3**.

The dienone **3** was extremely prone to spontaneous polymerization, and it was therefore surprising to find that with 30% H_2O_2 it formed a stable hemi-hydrogen peroxide complex. This complex (mp 52–54 °C) exhibited spectral characteristics identical with **3** with these exceptions: IR ($CHCl_3$) 3250 cm^{-1} (br); ^1H NMR (Me_2SO-d_6) δ 9.68 (s, H_2O_2); MS m/e 34 (H_2O_2). It dissolved readily in common organic solvents and could be recovered from them unchanged. This stable complex provided us with an excellent means of storing methylenomycin B (**3**). Solvent extraction of an aqueous solution of the H_2O_2 complex readily afforded **3**.

Hornemann[9] recently isolated compound **8** from the bacterial broth that produced methylenomycin A (**1**) and showed that **8** is a precursor to **1**. In view of the known



8

tendency of vinylogues of β-keto acids to undergo decarboxylation at relatively moderate temperatures, it is not unlikely that **3** is actually a chemical decomposition product of **8** formed during the original isolation process.

Acknowledgment. The authors wish to thank Dr. E. P. Oliveto for his interest and stimulating discussions of this work. We also wish to thank Dr. W. Benz, Dr. V. Toome, and Mr. S. Traiman for mass, UV, and IR spectra, respectively, as well as Dr. J. F. Blount for X-ray structural determination and Dr. F. Scheidl for microanalyses.

Registry No. **2**, 52775-77-6; **3**, 52775-77-6; **3** hemihydrogen peroxide, 71719-41-0; **4**, 1121-05-7; **5**, 71719-42-1; **6**, 71719-43-2; **7**, 71719-44-3; 2-hydroxy-3-methylcyclopent-2-en-1-one, 80-71-7; 2-*N*-pyrrolidino-5-methylcyclopent-2-en-1-one, 4933-43-1; pyrrolidine, 123-75-1; methyl iodide, 74-88-4.

Supplementary Material Available: Experimental Section providing preparation details for the compounds in the text (7 pages). Ordering information is given on any current masthead page.

(9) Dr. U. Hornemann, Purdue University, Indiana, personal communication. We wish to thank Dr. Hornemann for communicating his results to us. See U. Hornemann and D. A. Hopwoods, *Tetrahedron Lett.*, 2977 (1978).

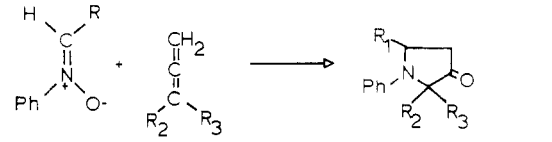
Jane Jernow,* William Tautz, Perry Rosen Thomas H. Williams

Chemical Research Department
Hoffmann-La Roche Inc.
Nutley, New Jersey 07110
Received June 26, 1979

Intermolecular Allene–Nitrone Cycloadditions

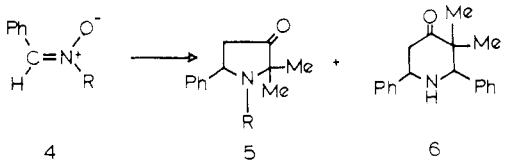
Summary: An intermolecular cycloaddition of *C,N*-diphenylnitrone with allene is described which affords three monoadducts, including a pyrrolidinone, an isoxazolidine, and a tetrahydrobenzazapinone.

Sir: The reaction of a nitrone with a cumulatively unsaturated system was first investigated by E. Beckmann[1] in 1890 and involved the addition of *N*-benzylidenebenzylamine *N*-oxide to phenyl isocyanate. In the intervening 89 years, nitrone cycloadditions involving isothiocyanates, carbon disulfide, allenes, ketenes, ketene imines, and carbodiimides have undergone some study.[2] LeBel[3] investigated the intramolecular cycloaddition reactions of allenic nitrones and, indeed, two reports[4,5] have focused on the intermolecular reactions of nitrones with simple allenes. Thus *C*-benzoyl-*N*-phenylnitrone (**1a**) was reported[4] to provide the 3-pyrrolidinone **3a** in 85% yield as the sole product isolated upon reaction with allene, while *C,N*-diphenylnitrone (**1b**) gave **3b** upon reaction with 1,1-dimethylallene (**2b**). In addition to the 3-pyrrolidinones



1a, R_1=COPh 2a, R_2=R_3=H 3a, R_1=COPh, R_2=R_3=H
b, R_1=Ph b, R_2=R_3=Me b, R_1=Ph, R_2=R_3=Me

obtained from the reaction of *N*-arylnitrones with allenes, *N*-alkylnitrones also are reported[5] to afford 4-piperidinones (e.g., **6**) upon reaction with dimethylallene.



4 **5** **6**

In contrast with the results noted above, we find that the reaction of *C,N*-diphenylnitrone (**1b**) with excess allene in a sealed tube at 72 °C for 60 h leads to the formation of three products. After opening the reaction vessel at −78

(1) E. Beckmann, *Ber. Dtsch. Chem. Ges.*, **23**, 1680, 331 (1890); **27**, 1957 (1894).
(2) For an excellent review of such transformations, see D. St. C. Black, R. F. Crozier, and V. C. Davis, *Synthesis*, **7**, 205 (1975).
(3) N. A. LeBel and E. Banucci, *J. Am. Chem. Soc.*, **92**, 5278 (1970).
(4) M. C. Aversa, G. Cum, and N. Uccella, *J. Chem. Soc., Chem. Commun.*, 156 (1971).
(5) G. Cum, G. Sindona, and N. Uccella, *J. Chem. Soc., Perkin Trans. 1*, 719 (1976).

0022-3263/79/1944-4213$01.00/0