tion and it would not be surprising if the TPP system were more flexible.

Zinc–nitrogen bond lengths vary from 2.03 to 2.23 Å.[1c,9,10] This would place the zinc 0.30–0.50 Å out of the plane of the porphyrin ring.

Our results for the conformation of metalloporphyrins in solution agree qualitatively with results obtained by X-ray crystallographic methods. It appears that the conformation of the metalloporphyrin is determined by the number of extra planar ligands; no ligands, essentially planar; one ligand, metal out of the plane toward the ligand; two ligands, essentially planar.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(10) P. C. Tain, E. C. Lingafetter, and P. Paoletti, *J. Amer. Chem. Soc.*, 90, 519 (1968).

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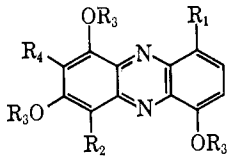
Lomofungin. I. Degradative Studies of a New Phenazine Antibiotic

Sir:

The recently described antibiotic lomofungin[1] has been reported to inhibit the growth of gram-positive and gram-negative bacteria as well as fungi. We assign here structure **1** (1-carbomethoxy-5-formyl-4,6,8-trihydroxyphenazine) to the antibiotic.

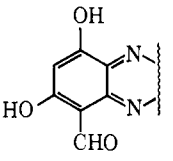


1, R_1 = $COOCH_3$; R_2 = CHO; R_3 = R_4 = H
2, R_1 = $COOCH_3$; R_2 = $CH(OCOCH_3)_2$; R_3 = $COCH_3$; R_4 = H
3, R_1 = $COOCH_3$; R_2 = CHO; R_3 = CH_3; R_4 = H
4, R_1 = $COOCH_3$; R_2 = CH_2OH; R_3 = CH_3; R_4 = H
5, R_1 = $COOCH_3$; R_2 = CH_2OCH_3; R_3 = CH_3; R_4 = H
6, R_1 = $COOCH_3$; R_2 = H; R_3 = CH_3; R_4 = H
7, R_1 = $COOCH_3$; R_2 = CHO; R_3 = R_4 = CH_3
8, R_1 = COOH; R_2 = CHO; R_3 = CH_3; R_4 = H
9, R_1 = COOH; R_2 = CH_2OCH_3; R_3 = CH_3; R_4 = H
10, R_1 = H; R_2 = CH_2OCH_3; R_3 = CH_3; R_4 = H
11, R_1 = R_2 = R_3 = CH_3; R_4 = H

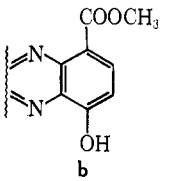
Lomofungin is indicated to be highly aromatic by its molecular formula ($C_{15}H_{10}N_2O_6$;[2a,b] confirmed by high-resolution mass spectrometry), is limited to a linear three-ring system[3] by the electronic spectrum ($\lambda\lambda_{max}$ 257, 364 mμ, $\epsilon\epsilon_{max}$ 72,500, 19,000, respectively) of its acetylation product (**2**; $C_{25}H_{22}N_2O_{12}$;[2a] mp 166–168°), formed at room temperature in pyridine–acetic anhydride or in acetic anhydride–sulfuric acid, and is defined as a phenazine by oxidation of the antibiotic with refluxing concentrated nitric acid to 2,3,5,6-pyrazinetetracarboxylic acid, characterized as its tetramethyl ester [$C_{12}H_{12}N_2O_8$;[2a,b] single nmr peak in $CDCl_3$ at δ 4.05 s; mp 180–181° (lit. 181–182°)[4]].

Methylation of lomofungin with methyl iodide and silver oxide in chloroform at 40° gave its trimethyl ether **3** ($C_{18}H_{16}N_2O_6$;[2a,b] mp 215–217°), whose nmr spectrum[5] contains three new $ArOCH_3$ singlets at δ 4.14, 4.17, and 4.23. In addition to these three phenolic hydroxyl groups lomofungin contains as functional groups an aldehyde and a methyl ester.

The aldehyde group is indicated by reduction of **3** with sodium borohydride in methanol to **4** ($C_{18}H_{18}N_2O_6$;[2a,b] mp 222–225°; $-CH_2O-$ singlet at δ 5.39), accompanied by its aliphatic methyl ether **5** ($C_{19}H_{20}N_2O_6$;[2a,b] mp 177–178°; $ROCH_3$ singlet at δ 3.52). The substitution pattern of the ring bearing the formyl group is defined as shown in **1** by decarbonylation of **3**, employing chlorotris(triphenylphosphine)rhodium(I),[6] to give **6** ($C_{17}H_{16}N_2O_5$;[2a,b] mp 180–182°), whose nmr spectrum contains an aromatic *meta*-AB quartet (δ 6.87 and 7.32; J = 2.5 Hz) in place of the one-proton singlet (δ 6.91) of **3**. Since the aromatic proton generated on decarbonylation is that at lower field (δ 7.32) the formyl group is placed as shown (α) rather than between the two methoxyl groups (β). Isolation of a fully aromatic C-methylated side reaction product **7** ($C_{19}H_{18}N_2O_6$;[2a,b] mp 240–243°; $ArCH_3$ singlet at δ 2.44) from the above methylation of lomofungin also indicates a vacant position between the hydroxyl groups of **1**. These results define unit **a** in the antibiotic.



a



b

The methyl ester function is defined by saponification of **3** to give **8** and of **5** to give **9** ($C_{18}H_{18}N_2O_6$;[2a,b] mp 231–234°), and is located by decarboxylation of **9** over copper powder in pyridine at 220° to give **10** ($C_{17}H_{18}N_2O_4$).[2b] The nmr spectrum of the latter compound (**10**) shows the presence of three aromatic protons on adjacent carbons (δ 7.03, J = 7.96, 1.22 Hz; δ 7.64, J = 7.96, 8.56 Hz; δ 7.95, J = 8.56, 1.22 Hz), while its precursor **9** shows an *ortho*-substitution pattern (δ 7.16, 8.67; J = 8.0 Hz). Since H-1 in the spectrum of **10** must be the proton at δ 7.95, the expected deshielding effect of the carboxyl group is only consistent with its placement at C-1 in **9** (H-2 at δ 8.67 in **9** *vs.* δ 7.64 in **10**; H-3 at δ 7.16 in **9** *vs.* δ 7.03 in **10**) and this placement is consistent with the similar J_{23} coupling constants in the two compounds (8.0 Hz in **9**, 7.96 Hz in **10**). The ring containing the carbomethoxy group is thus unit **b**.

The substitution patterns of the terminal rings are supported by the nmr spectrum of **11** ($C_{17}H_{18}N_2O_3$,[2a] mp 238°), obtained by prolonged lithium aluminum hydride reduction of **3** in refluxing tetrahydrofuran. In the

(1) M. E. Bergy and L. E. Johnson, U. S. Patent 3,359,165 (1967); *Chem. Abstr.*, **68**, 38164y (1968). In the patent the name lomondomycin is used for lomofungin.

(2) (a) Mass spectra, obtained on an Atlas CH4 mass spectrometer by the direct inlet technique, employing an oven inlet lock, were in agreement with the formula cited. (b) Elemental analyses agree with the formula given.

(3) *Cf.*, *i.a.*, L. Birkofer, *Chem. Ber.*, **85**, 1023 (1952); J. A. Van Allan, G. A. Reynolds, and R. E. Adel, *J. Org. Chem.*, **27**, 1659 (1962); M. Ikekawa, *Chem. Pharm. Bull.* (Tokyo), **6**, 401 (1958); K. L. Rinehart, Jr., and H. B. Renfroe, *J. Amer. Chem. Soc.*, **83**, 3729 (1961).

(4) T. Asao, *Bull. Chem. Soc. Jap.*, **34**, 151 (1961).

(5) Nmr spectra were determined on deuteriochloroform solutions; chemical shifts are expressed in parts per million relative to internal tetramethylsilane (δ = 0).

(6) J. Tsuji and K. Ohno, *Tetrahedron Lett.*, 2173 (1967).

nmr spectrum of **11** one of the aryl methyl groups (δ 2.84 d, J = 1.0 Hz) is slightly split by an adjacent aromatic proton (δ 7.45 octet, J = 8.0, 1.0 Hz), while the second aryl methyl (δ 2.73 s), found at nearly identical field but with no adjacent hydrogens, is unsplit. Of the two theoretically possible combinations of units **a** and **b**, that represented in **1** is chosen over the alternative, 1-carbomethoxy-8-formyl-4,5,7-trihydroxyphenazine, on biosynthetic grounds, since we presume lomofungin to arise from oxidative coupling of 2 mol of 4-hydroxyanthranilic acid. In this connection it is significant that a similar substitution pattern is found in the antibiotic griseolutein A.[7]

Synthetic experiments in the lomofungin series will be described in a subsequent report.[8]

Acknowledgment. This work was supported in part by a research grant (No. AI 01278) from the National Institute of Allergy and Infectious Diseases.

(7) S. Nakamura, *J. Antibiot. (Tokyo)*, **A12**, 55 (1957).

(8) NOTE ADDED IN PROOF. Compound **11** has now been prepared by an unequivocal route.

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Mechanism of Thermal Decomposition of *n*-Butyl(tri-*n*-butylphosphine)copper(I)[1]

Sir:

Alkyllithium,[2]-magnesium,[2] and -aluminum[3] reagents react rapidly with transition metal salts, yielding mixtures of hydrocarbons believed to be derived from the thermal decomposition of intermediate transition metal σ-alkyls. Detailed mechanisms for the thermal decomposition of alkyl transition metal compounds have not been established. However, product mixtures from many of the reactions of main group σ-alkyls with transition metal salts contain approximately equal quantities of alkane and alkene. This observation has led to the suggestion that free alkyl radicals, derived from homolytic scission of carbon–metal σ bonds, are involved as reactive intermediates, and that alkane and alkene are derived from disproportionation of these alkyl radicals.[2] Our interest in these reactions and in the general area of mechanisms of thermal decomposition of transition metal organometallic compounds has prompted us to examine in detail the thermal decomposition of authentic *n*-butyl(tri-*n*-butylphosphine)copper(I) (**1**). Here we wish to summarize evidence indicating that the dominant pathway for thermal decomposition of this alkylcopper(I) compound to *n*-butane and 1-butene does *not* involve free *n*-butyl radicals, but rather occurs by a two-step process consisting of initial formation of 1-butene by β elimination of copper(I) hydride from **1**, followed by reduction of a second equivalent of **1** to *n*-butane by this copper(I) hydride.

$$\underset{\mathbf{1}}{CH_3CH_2CH_2CH_2CuP(n\text{-}Bu)_3} \longrightarrow CH_3CH_2CH{=}CH_2 + HCuP(n\text{-}Bu)_3 \quad (1)$$

$$CH_3CH_2CH_2CH_2CuP(n\text{-}Bu)_3 + HCuP(n\text{-}Bu)_3 \longrightarrow CH_3CH_2CH_2CH_3 + 2Cu^0 + 2P(n\text{-}Bu)_3 \quad (2)$$

Typically, **1** was prepared by reaction of 0.25 mmol of $[ICuP(n\text{-}Bu)_3]_4$ with 1.0 mmol of *n*-butyllithium (15% in hexane) in 10 ml of ether at −78° followed by separation of lithium iodide from the resulting light yellow solution by precipitation with 1.1 mmol of dioxane.[4,5] Compound **1** has not been isolated;[4] however, analysis of its solutions indicates an empirical composition $(C_4H_9)_{0.97\pm0.02}Cu_{1.00}P(n\text{-}Bu_3)_{1.02\pm0.03}$, with 1.7 ± 0.1% Li and <0.5% I based on copper remaining in solution. Thermal decomposition of **1** is complete in 4 hr at 0° in ether solution, yielding copper metal, tri-*n*-butylphosphine, 1-butene (51%) *n*-butane (49%), and hydrogen (10%); less than 0.1% *n*-octane is formed. Hydrolysis of the solution remaining at the conclusion of the thermal decomposition yields an additional 8% hydrogen. Control experiments have demonstrated that the hydrocarbon products are not derived from the tri-*n*-butylphosphine ligands: the thermal decomposition of *n*-butyl(tri-*n*-octylphosphine)copper(I) yields no octane, and that of *n*-butyl-2,2-d_2-(tri-*n*-butylphosphine)copper(I) (**2**) yields no butane-d_1, butane-d_0, or butene-d_0.

The absence of octane among the products of decomposition of **1** is sufficient to establish that butane and 1-butene are not formed by disproportionation of *n*-butyl radicals, since the ratio of rate constants for the disproportionation and combination of these radicals falls in the range 0.1–0.2.[6] In addition, the ratio of the yields of *n*-butane and 1-butene formed on thermal decomposition of **1** is invariant to the hydrogen-donor ability of the solvent: almost identical ratios are observed in ether, *n*-hexane, and 9:1 v/v *n*-hexane–cumene solutions. Moreover, thermal decomposition of the related copper(I) reagent hex-5-enyl(tri-*n*-butylphosphine)copper(I) in ether yields 44% 1-hexene, 52% 1,5-hexadiene, and only 3.5% cyclized hydrocarbons.[7] Taken together, these data effectively preclude the important involvement of *n*-alkyl radicals derived from homolytic scission of the carbon–copper(I) σ bonds of **1** during its thermal decomposition.

Both the detection of hydrogen among the products of thermal decomposition of **1** and the formation of additional hydrogen on acidification of the solution remaining after complete decomposition implicate a copper hydride[8] as an intermediate in the reaction. The formation of significant quantities of "CuH" during decomposition of **1** was confirmed using isotopic dilution techniques. Partial decomposition (10 min, 0°,

(1) Supported by the National Science Foundation, Grants 7266 and 14247, and by the International Copper Research Association, Inc.

(2) H. Gilman, R. G. Jones, and L. A. Wood, *J. Amer. Chem. Soc.*, **76**, 3615 (1954); M. H. Abraham and M. J. Hogarth, *J. Organometal. Chem.*, **12**, 1 (1968); W. B. Smith, *J. Org. Chem.*, **26**, 4206 (1961); F. W. Frey, Jr., *ibid.*, **26**, 5187 (1961); M. S. Kharasch, *et al.*, *ibid.*, **21**, 322 (1956).

(3) M. I. Prince and K. Weiss, *J. Organometal. Chem.*, **2**, 166 (1964).

(4) For experimental procedures, see G. M. Whitesides, W. F. Fischer, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *J Amer. Chem. Soc.*, **91**, 4871 (1969), and references therein.

(5) Although the degree of association of **1** is not known, it is assumed to be aggregated; see L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler, and K. Knox, *ibid.*, **90**, 7357 (1968), for references to relevant structures. The reactions represented by eq 1 and 2 probably take place within the confines of common copper atom clusters.

(6) N. E. Morganrath and J. G. Calvert, *ibid.*, **88**, 5387 (1966); A. P. Stefani, *ibid.*, **90**, 1694 (1968), and references in each.

(7) Cyclization of the 5-hexenyl radical is more rapid than hydrogen atom abstraction from ether solvents: *cf.* C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *J. Amer. Chem. Soc.*, **88**, 5361 (1966); J. F. Garst and F. E. Barton, *Tetrahedron Lett.*, 587 (1969).

(8) (a) G. M. Whitesides, J. San Filippo, Jr., E. R. Stedronsky, and C. P. Casey, *J. Amer. Chem. Soc.*, **91**, 6542 (1969); (b) J. A. Dilts and D. F. Shriver, *ibid.*, **90**, 5769 (1968); **91**, 4088 (1969).