Notes

Observations on the Synthesis and Spectroscopic Characteristics of Purpurins

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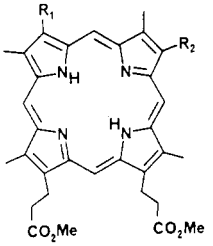
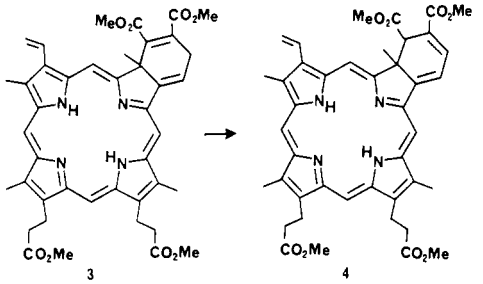
Visible spectroscopy can be a powerful tool in porphyrin chemistry for detecting changes in the chromophore of the macrocycle, brought about, for example, by the introduction of peripheral groups (e.g., carbonyl, vinyl) capable of extending the conjugated system. One of the results of such a change is a shift to higher wavelength of the absorption of band I in the porphyrin visible spectrum.[1] This can be illustrated by observing the bathochromic shift of band I of deuteroporphyrin IX dimethyl ester (**1**, λ_{max} 621 nm) on introduction of an acyl group to give 2(4)-monoacetyldeuteroporphyrin IX dimethyl ester (**2**, λ_{max} 634 nm).[2] Similarly, when the chlorin **3** formed by Diels–Alder



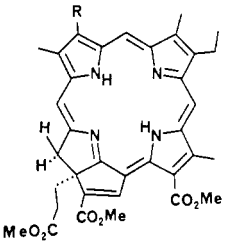
1 $R_1 = R_2 = H$
2 $R_1 = H$ $R_2 = COCH_3$
$R_1 = COCH_3$ $R_2 = H$

addition of dimethyl acetylenedicarboxylate to protoporphyrin IX dimethyl ester is treated with base, the isolated double bond tautomerizes to the fully conjugated system **4**, accompanied again by a red shift in the visible spectrum of band I (from 663 to 688 nm).[3]



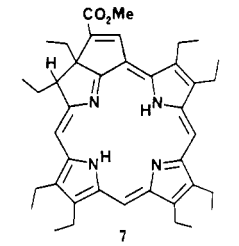
3 **4**

As part of our research into chemical transformations of porphyrins, we required a convenient method for monitoring purpurin formation and subsequent reactions on these macrocycles.[4] We anticipated that the unique chromophore of these systems would show characteristic spectroscopic properties. Only few literature examples are available for comparative purposes. In all, three purpurins of related structure have been reported.[5,6,7] Purpurin **5** contains a chromophore influenced by extended conjugation through a methoxycarbonyl group at C-13. Chemical



5 $R = CH_2CH_2NHCOCH_3$
6 $R = CH{=}CH_2$

modification of the C-3 (*N*-acylamino)ethyl moiety of **5** to a vinyl group resulted in a macrocycle **6**, in which the parent chromophore was extended through two peripheral substituents. Following this reaction by visible spectroscopy, there was, as expected, a shift to higher wavelength of the absorption of band I from 705 (in **5**) to 714 nm (in **6**).[5] The octaethylpurpurin, **7**, which contains only the



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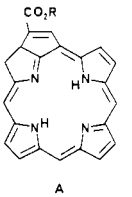
purpurin chromophore, would be expected to show an absorption of band I in the visible spectrum, at a wavelength significantly below 705 nm. We were surprised, however, to find a reported value of 704 nm for this absorption[6]—much higher than had been anticipated. We decided, therefore, to investigate these systems further in an attempt to determine the diagnostic value of the visible spectra of purpurins in general.

(1) (a) Band I in the visible spectra of porphyrin macrocycles refers to the absorption at highest wavelength, and is also known as the α or Q(0,0) band. (b) Goutermann, M. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, pp 1–165.

(2) Fuhrhop, J.-H.; Smith, K. M. In "Laboratory Methods in Porphyrin and Metalloporphyrin Research"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; p 125.

(3) Morgan, A. R.; Pangka, V. S.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1984**, 1047–1048.

(4) In this paper, we limit the definition of the term purpurin to include only porphyrin macrocycles having the parent ring structure A.



A

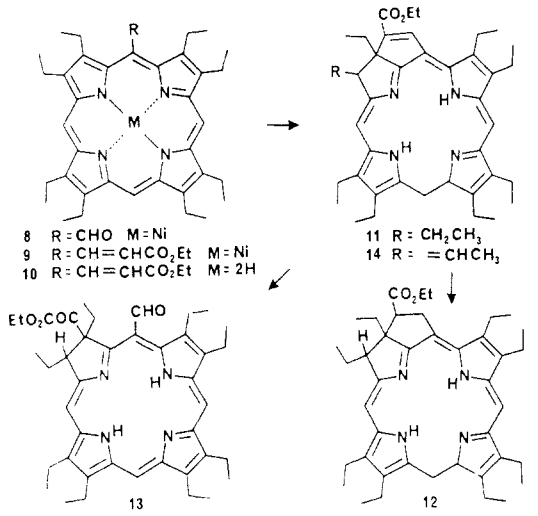
(5) Woodward, R. B.; Ayer, W. A.; Beaton, J. M.; Bickelhaupt, F.; Bonnett, R.; Buchschacher, P.; Closs, G. L.; Dutler, H.; Hannah, J.; Hauck, F. P.; Itô, S.; Langemann, A.; LeGoff, E.; Leimgruber, W.; Lwowski, W.; Sauer, J.; Valenta, Z.; Volz, H. *J. Am. Chem. Soc.* **1960**, *82*, 3800–3802.

(6) Arnold, D. P.; Gaete-Holmes, R.; Johnson, A. W.; Smith, A. R. P.; Williams, G. A. *J. Chem. Soc. Perkin Trans. 1* **1979**, 1660–1670.

(7) Fuhrhop, J.-H.; Witte, L. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 361–362.

0022-3263/86/1951-1347$01.50/0

Scheme I



Results and Discussion

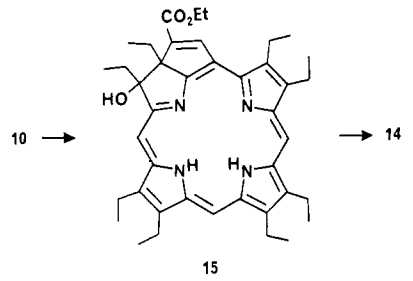
According to the method of Johnson and co-workers[6] (Scheme I), nickel *meso*-formyloctaethylporphyrin **8** was treated with (carbethoxymethylene)triphenylphosphorane to give nickel *meso*-[β-(ethoxycarbonyl)vinyl]octaethylporphyrin **9**. Subsequent demetalation with concentrated sulfuric acid (to yield the porphyrin free base **10**) and cyclization in refluxing glacial acetic acid under a nitrogen atmosphere afforded the corresponding (ethoxycarbonyl)octaethylpurpurin **11** in good yield. Evidence supporting the formulation of **11** was given by mass spectrometry, which indicated a product isomeric with the reactant, and by the ^{1}H NMR spectrum of **11**. Thus, the signals associated with the acrylate protons in **10** (doublets at δ 10.40, 6.20) were no longer present in the spectrum of the product, which contained instead a one proton singlet at δ 9.40 attributable to the olefinic proton of the cyclopentenyl ring. Of the four meso protons, one is now adjacent to a reduced pyrrole ring, and this is clearly seen by the expected upfield shift of one of the resonances to δ 8.71.[8] In addition, both the methyl and methylene resonances of a peripheral ethyl group exhibit upfield shifts of approximately 1 ppm, consistent with their presence on a nonplanar reduced pyrrolic ring.[9] Finally, the visible spectrum of the product gave a purpurin-type spectrum, with the absorption of band I appearing at 695 nm—a value contrary to that reported for the corresponding methyl ester **7** but in complete agreement with the anticipated value based on observations on extended purpurin chromophores, as described above. The spectroscopic formulation of the product as **11** was supported by the following chemical transformations.

Catalytic hydrogenation of **11** with 5% Pd/C resulted in reduction of the molecule to the porphyrinogen state, as evidenced by the absence of color in the resulting solution. Filtration to remove the catalyst followed by vigorous stirring in the presence of air quickly reoxidized the macrocycle, but not the cyclopentane ring, giving a deep blue/green solution from which the product **12** was isolated in good yield. The formulation of the product as **12** is based on its mass spectrum (confirming addition of 1 mol of hydrogen), its visible spectrum, which resembled that of a chlorin[10] (λ_{max} 662 nm), and its ^{1}H NMR spectrum, which confirmed the integrity of the carbon skeleton but lacked the signal attributable to a cyclopentenyl proton. The ease of reduction of the cyclopentenyl ring of **11** was complemented by its ease of oxidation. Thus, stirring a solution of **11** in air in the presence of strong sunlight resulted in cleavage of the isocyclic double bond, to yield a product formulated by its spectroscopic properties as the aldehyde **13**. The absence of an olefinic proton resonance in the ^{1}H NMR spectrum of **11** and the appearance of a resonance at δ 11.66 assignable to an aldehyde proton together with resonances indicating the retention of the reduced pyrrole moiety (meso proton at δ 8.68, upfield shift in ethyl resonances) confirm the structure of **13**. In addition, the visible spectrum indicated that band I had shifted to lower wavelength (690 nm), an observation similar to that reported during the corresponding oxidation of purpurin **6**.[5] Further information on the facile oxidation of these systems was obtained when cyclization of **10** was performed in the presence of air. Following the course of the reaction by visible spectroscopy, two absorptions of equal intensity (695, 711 nm) appeared as the reaction proceeded, suggesting the formation of two products. This was confirmed by TLC of the reaction mixture on silica with 2% methanol in dichloromethane when two major green bands were seen (R_f values 0.3, 0.4). Separation and purification resulted in isolation of equal amounts of each product, of which the less mobile fraction (by TLC) was shown to be identical with purpurin **11** formed during cyclization of **10** under a nitrogen atmosphere. The identity of the second product was established by spectroscopic and chemical techniques, as described below.

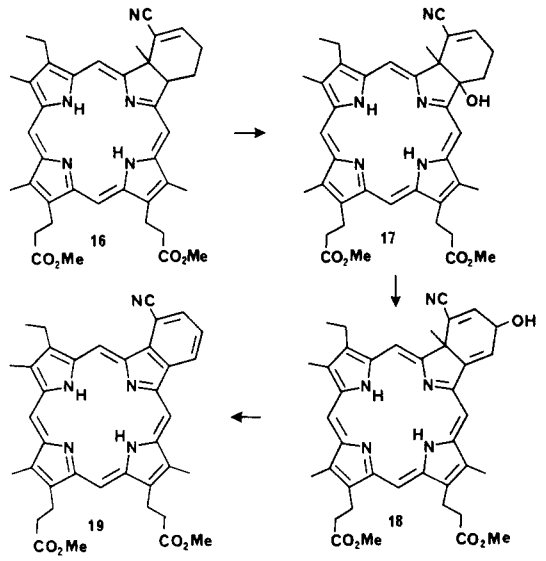
^{1}H NMR studies revealed the presence of a cyclopentenyl ring (resonances attributable to olefinic proton, and ethyl group of reduced pyrrole ring) and also showed a three-proton doublet at δ 2.32 and a quartet at δ 7.23. Decoupling experiments indicated that these latter two signals were related and strongly suggested the presence of a $CHCH_3$ moiety in the product. In addition, NOE enhancement of one meso proton resonance was observed, a point we address below. Mass spectrometry indicated a molecular weight of 630 daltons, i.e., 2 mass units less than purpurin **11**, while visible spectroscopy gave an absorption of band I at 711 nm, which on the basis of prior arguments indicated that the purpurin chromophore had been extended through conjugation at the periphery of the macrocycle. These spectroscopic data allow unambiguous assignment of structure **14** to the product of this reaction. Chemical proof of the relationship between purpurins **11** and **14** came from catalytic hydrogenation of **14** under conditions similar to those described above. Aerial oxidation of the porphyrinogen intermediate resulted in isolation of a product which proved to be identical with that obtained from the corresponding reaction of **11**. In the former case, the chlorin **12** arises from the addition of 2 mol of hydrogen to purpurin **14** and confirms the interpretation of the spectroscopic data for this compound. The isolation of **14** can be readily explained by initial formation of the C-2 epimers of purpurin **11**. Woodward and coworkers, during the preparation of purpurin **5**, described the isolation of only the 17,18-trans isomer,[5] which could indicate rapid conversion of the kinetically favored epimer into the thermodynamically favored isomer. In the presence of air, the less stable isomer may be trapped as its 2-hydroxy derivative **15** which under reaction conditions dehydrates to the purpurin **14** (Scheme II). Such a process explains why both purpurins **11** and **14** are formed in equal

(8) Bonnett, R.; Stephenson, G. F. *J. Chem. Soc. C* **1966**, 1600–1604.
(9) Chang, C. K. *Biochemistry* **1980**, *19*, 1971–1976.
(10) Scheer, H.; Inhoffen, H. H. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 11, pp 45–85.

Scheme II



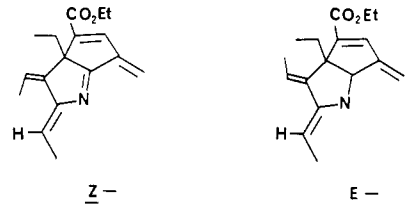
Scheme III



amounts and also accounts for the observation that the isolated purpurin **11** is unaffected when refluxed in glacial acetic acid in the presence of air or when treated with a base such as triethylamine or 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU).

Such oxidations at the periphery of a reduced porphyrin macrocycle have, in fact, recently been reported.[4] The formation of the monobenzoporphyrin **19** from the chlorin **16** is thought to proceed by two successive aerial oxidations via the intermediates **17** and **18** (Scheme III), an observation closely related to the reaction described above.

One final note involves the relative stereochemistry about the exocyclic double bond of **14**. During NOE studies described above, on the macrocycle, irradiation of the methyl doublet resonance at δ 2.50 not only led to collapse of the methylene quartet at δ 7.23 but also resulted in enhancement of the highest field meso resonance at δ 9.00. This is consistent with a *Z* configuration about the double bond, and we, therefore, tentatively assign this configuration to purpurin **14**.



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Experimental Section

Visible spectra were recorded on a Beckman Acta III spectrometer; absorptions are given in nanometers (solutions in dichloromethane). Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained on a JEOL FX-90Q spectrometer; chemical shifts are expressed in parts per million downfield from internal tetramethylsilane. Low-resolution mass spectra were measured (direct insertion probe) on a Hewlett-Packard 5987 mass spectrometer. Analytical TLC was performed by using Merck silica gel 60F 254 precoated sheets (0.2 mm); preparative chromatography was performed on a chromatotron,[11] using Merck silica gel 60PF 254 with $CaSO_4 \cdot {}^1/_2H_2O$ (catalog no. 7749). Melting points are uncorrected. Elemental analyses were performed by MicAnal, Tucson, AZ 85717.

Nickel *meso*-[β-(Ethoxycarbonyl)vinyl]octaethylporphyrin (9). A solution of nickel *meso*-formyloctaethylporphyrin (**8**)[12] (506 mg) and (carbethoxymethylene)triphenylphosphorane (1.024 g) in xylene (50 mL) was heated under reflux for 18 h. The solution was cooled, the solvent removed in vacuo, and the resulting solid chromatographed on silica by using dichloromethane for elution. A minor fraction of nickel OEP was collected first, followed by a major red band. Collection, removal of solvent, and crystallization of the resulting residue from dichloromethane–methanol gave the product **9** as small brown needles (455 mg, 81% yield): vis λ_{max} 405, 530, 565 nm (ϵ 94 180, 18 604, 27 790); ^{1}H NMR ($CDCl_3$) δ 10.14 (d, J = 17 Hz, 1 H, β-H of acrylic ester), 9.49 (s, 3 H, meso H), 5.32 (d, J = 17 Hz, 1 H, α-H of acrylic ester), 4.43 (q, 2 H, CH_2 of ester), 3.86 (q, 16 H, CH_2 of peripheral ethyl), 1.81 (m, 24 H, CH_3 of peripheral ethyl), 1.37 (t, 3 H, CH_3 of ester).

***meso*-[β-(Ethoxycarbonyl)vinyl]octaethylporphyrin (10).**[13] A solution of the nickel complex **9** (621 mg) was dissolved in concentrated sulfuric acid (10 mL) and kept for 2 h at room temperature. Dichloromethane (100 mL) was added, followed by saturated aqueous sodium hydrogen carbonate. After neutralization, the organic layer was collected, washed, and dried and the solvent removed. Crystallization of the crude product from dichloromethane–methanol gave the product **10** as small reddish brown crystals (552 mg 100% yield), having spectroscopic properties identical with those previously reported.[13]

Cyclization of *meso*-[β-(Ethoxycarbonyl)vinyl]octaethylporphyrin to 11. A solution of *meso*-[β-(ethoxycarbonyl)vinyl]octaethylporphyrin (**10**) (100 mg) in glacial acetic acid (20 mL) was heated under reflux in a nitrogen atmosphere for 24 h. After the mixture was cooled, the solvent was removed in vacuo and replaced with dichloromethane. Chromatography on silica with dichloromethane as eluant gave a major green fraction. Removal of the solvent and crystallization from dichloromethane–methanol gave purple microcrystals of the product **11** (68 mg, 68% yield): mp 135–138 °C; vis λ_{max} 433, 453, 503, 530, 568, 648, 695 nm (ϵ 89 509, 89 509, 14 571, 12 143, 18 908, 10 582, 42 673); ^{1}H NMR ($CDCl_3$) δ 9.47, 9.44, 8.71 (all s, 3 H, meso H), 9.40 (s, 1 H, H of isocyclic ring), 4.53 (q, 2 H CH_2 of ester), 3.80 (m, 13 H, CH_2 of peripheral ethyl, C-2 H), 3.20, 2.64 (m, 4 H, CH_2 of 1,2-ethyl), 1.72 (m, 24 H, CH_3 of peripheral ethyl, CH_3 of ester), –0.28 (t, CH_3 of 3-ethyl), –0.98 (s, 2 H, NH); mass spectrum, *m/e* 632 (M^+). Anal. Calcd for $C_{41}H_{52}N_4O_2 \cdot 1.5H_2O$: C, 74.65; H, 8.64. Found: C, 74.37, H, 8.87.

Zinc Complex. Zinc acetate (100 mg) was added to a solution of purpurin **11** (20 mg) in dichloromethane (15 mL)–methanol (5 mL) and the mixture refluxed until chelation was complete (monitored by electronic spectrum; ca. 4 min). The resulting solution was concentrated (to 7 mL) and the precipitated zinc complex of **11** filtered. Recrystallization of the product from dichloromethane–methanol yielded microcrystals (18 mg 82% yield): vis λ_{max} 413, 435, 535, 578, 618, 663 nm (ϵ 195 270, 219 498, 14 052, 18 866, 28 588, 85 733).

5-Formyl-2-(ethoxyoxalyl)octaethylchlorin (13). A solution of the purpurin **11** (30 mg) in dichloromethane (100 mL) was stirred in Toledo sunlight for 4.5 h. Removal of solvent in vacuo and chromatography of the residue on silica with dichloromethane for elution gave a major brown band, which was collected. Removal of solvent and crystallization from dichloromethane–methanol gave brown microprisms of the aldehyde **13** (23 mg 74% yield): mp 122–125 °C; vis λ_{max} 413, 510, 545, 640, 690 nm (ϵ 99 947,

(11) The chromatotron is available from Harison Research, Palo Alto, CA 94306.

(12) Grigg, R.; Shelton, G.; Sweeney, A.; Johnson, A. W. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1789–1798.

(13) Fuhrhop, J.-H.; Witte, L.; Sheldrick, W. S. *Ann. Chem.* **1976**, 1537–1559.

9412, 7619, 5827, 34287); ^{1}H NMR ($CDCl_3$) δ 11.66 (s, 1 H, CHO), 9.55, 9.33, 8.68 (all s, 3 H, meso H), 4.75 (m, 1 H, 2-H), 4.12 (q, 2 H, CH_2 of ester), 3.70 (m, 12 H, CH_2 of peripheral ethyl), 2.67 (m, 4 H, CH_2 of 1,2-ethyl), 1.70 (t, 21 H, CH_3 of peripheral ethyl), 1.13 (t, 3 H CH_3 of ester), -0.46 (t, 3 H, CH_3 of 3-ethyl); mass spectrum, m/e (relative intensity) 664 (M^+, 12), 604 (11), 563 (41), 548 (100). Anal. Calcd for $C_{41}H_{52}N_4O_4 \cdot H_2O$: C, 72.14; H, 7.92. Found: C, 71.86; H, 8.01.

Hydrogenation of Purpurin 11. Palladium on charcoal (10%) (20 mg) was added to a stirred solution of purpurin 11 (100 mg) in tetrahydrofuran (20 mL) containing triethylamine (2 drops) and the resulting mixture hydrogenated at room temperature, under a slight positive pressure. After 5 h, the reaction mixture was filtered and the clear solution obtained vigorously stirred in air for 2.5 h. After complete oxidation of the intermediate porphyrinogen, indicated by a brown-colored solution and followed by measuring the intensity of an absorption at 660 nm in the visible spectrum of the solution, the solvent was removed in vacuo and the residue chromatographed on silica with 1% methanol in dichloromethane for elution. The major blue band was collected, the solvent removed, and the crude product crystallized from dichloromethane–methanol to give brown microprisms of **12**. (72 mg, 72% yield): mp 142–145 °C; vis λ_{max} 403, 500, 535, 558, 610, 660 nm (ϵ 114650, 23532, 5662, 4246, 8493, 39455); ^{1}H NMR ($CDCl_3$) δ 9.55, 8.68 (both s, 2:1, 3 H, meso H) 5.08–4.87 (m, 3 H, isocyclic CH_2, H), 4.70 (t, 1 H, 2-H), 4.45 (t, 2 H, CH_2 of ester), 3.80 (t, 12 H, CH_2 of peripheral ethyl), 2.90, 2.84 (m, 4 H, 1,2-ethyl), 1.74 (m, 21 H, CH_3 of peripheral ethyl), 1.54 (t, 3 H, CH_3 of ester), -0.23 (t, 3 H, CH_3 of 3-ethyl), -1.42, -2.02 (both s, 2 H, NH); mass spectrum, m/e 634 (M^+). Anal. Calcd for $C_{41}H_{54}N_4O_2 \cdot 2H_2O$: C, 73.43; H, 8.66. Found: C, 73.26; H, 8.66.

Zinc Complex. The zinc complex was prepared as described for the zinc complex of **11** in 92% yield: vis λ_{max} 408, 515, 545, 590, 633 nm (ϵ 145474, 9858, 5377, 15832, 59444).

Nickel Complex. The nickel complex was prepared in a similar manner in 86% yield: vis λ_{max} 405, 498, 533, 588, 630 nm (ϵ 145779, 11034, 8693, 19392, 64146).

Cyclization of *meso*-[β-(Ethoxycarbonyl)vinyl]octaethylporphyrin in Air to 14. *meso*-[β-(Ethoxycarbonyl)-vinyl]octaethylporphyrin (**10**) (100 mg) in glacial acetic acid (20 mL) was heated under reflux for 24 h. The solution was cooled, the solvent removed in vacuo, and the residue chromatographed on silica with dichloromethane for elution. The first major green band was collected, the solvent removed, and the crude product crystallized from dichloromethane–methanol to give deep purple microprisms of **14** (40 mg, 40% yield): mp 145–147 °C; vis λ_{max} 438, 510, 540, 583, 653, 715 nm (ϵ 104158, 9450, 11130, 15540, 9020, 42629); ^{1}H NMR ($CDCl_3$) δ 9.47, 9.40, 9.00 (all s, 3 H meso H), 9.30 (s, 1 H, H of isocyclic ring), 7.23 (q, 1 H), 4.56 (q, 2 H, CH_2 ester), 3.83 (m, 12 H, CH_2 of peripheral ethyl), 2.50 (d, 2 H, J = 8 Hz, CH=CH_3). 2.32 (m, 2 H, CH_2 of 3-ethyl), 1.62 (m, 21 H, CH_3 of peripheral ethyl), 0.215 (t, 3 H, CH_3 of 3-ethyl), -0.23, -0.69 (both s, 2 H, NH); mass spectrum, m/e (relative intensity) 630 (M^+ 100), 601 (79), 534 (43).

Zinc Complex. The zinc complex was prepared by the usual method in 95% yield: vis λ_{max} 430, 543, 593, 630, 680 nm (ϵ 141532, 6797, 8396, 14393, 41180).

A second major green band was also collected, the solvent removed, and the residue crystallized from dichloromethane–methanol to give purple microcrystals of purpurin **11** (39 mg, 39% yield), identical with an authentic sample.

Hydrogenation of 14. Purpurin **14** (100 mg) was hydrogenated under conditions similar to those described above to yield, after workup and chromatographic purification, chlorin **12** (65 mg, 65% yield), identical with an authentic sample.

Acknowledgment. Thanks are due to Bennett C. Borer and Jean L. Ensign for performing MS measurements at the GC/MS Analytical Services Laboratory of Bowling Green State University, OH 43403-0213.

Registry No. **8**, 52518-61-3; **9**, 99128-87-7; **10**, 61354-68-5; **11**, 99128-91-3; **11** (Zn complex), 99128-88-8; **12**, 99128-93-5; **12** (Zn complex), 99128-89-9; **12** (Ni complex), 99128-90-2; **13**, 99147-86-1; **14**, 99128-92-4; **14** (Zn complex), 99147-85-0; ethoxycarbonyl methylenetriphenylphosphorane, 1099-45-2.

Micellar Effects on Competitive Hydrolysis and Hydration of Vinylphosphonium Salts

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Vinyl phosphonium salts undergo reactions with $^-$OH in H_2O at C and P to give products of hydration and hydrolysis, respectively.[1] In a study[2] of phosphate ester hydrolysis under basic conditions catalyzed by micellar **2b**, we noted that **1b** displayed unusual C vs. P reactivity. Herein, we report a study of micellar effects on this competition with **1a–c**.[3]

At 25 °C, **1a** in ≤1.5 M NaOH yielded only **2a** from attack at C and in ≥2.0 M NaOH yielded a minor amount of **2a** (14%) and a mixture of products including **3a** (10%), **4a** (16%), **5a** (27%), and **6a** (17%) from attack at P (Chart I).[4] Thus, the regiochemistry depends on [$^-$OH]. In contrast, micellar **1b** displayed a distinctly different reactivity pattern. Predominant attack occurred at P in [$^-$OH]'s as low as 0.01 M but at C in [$^-$OH]'s ≤ 0.001 M. The former gave a complex mixture containing **3–6** and the latter **2b**. The behavior of **1c** paralleled that of **1a**, so the dependence of **1b**'s reactivity on [$^-$OH] manifests a micellar rather than a simple substituent effect.

These micellar effects represent a vivid example of the ability of cationic micelles to concentrate anionic reagents relative to the aqueous pseudophase.[6] Indeed, [$^-$OH] = 1–2 M is estimated[7] for the Stern layer of micellar **1b** in 0.01 M NaOH. For bimolecular reactions, the usual consequences of such concentration are catalysis or inhibition.[6] The results with **1b** represent a rare example of *regiochemical* consequences.[8] Indeed, there are only a few other reports[9] of such regio/chemoselectivity control.

(1) For examples, see: (a) Shutt, J. R.; Trippett, S. *J. Chem. Soc. C* **1969**, 2038. (b) Brophy, J. J.; Gallagher, M. J. *J. Chem. Soc., Chem. Commun.* **1967**, 344.

(2) Jaeger, D. A.; Bolikal, D. *J. Org. Chem.* **1985**, *50*, 4635.

(3) In some of the runs described below, $^-$OD–D_2O instead of $^-$OH–H_2O was actually used (see Experimental Section).

(4) (a) Shutt and Trippett[1a] reported that **1a** gives **3a**, **5a**, Ph_3PO, and Ph_3P (but not **4a** and **6a**) in aqueous 2 M NaOH at reflux. It was proposed that **3a** is formed by a rearrangement of **1a**, and **5a** via the addition of Ph_2PO^- to **1a**. In the present study, **5a** may result directly from the addition of Ph_2PO^- to **4a**, which is probably formed by a typical quaternary phosphonium salt hydrolysis:[5a] R_4P^+ $^-$OH → R_3PO + RH. (b) Hands and Mercer reported[5b] that $Ph_3P^+CH_2CH_2OH$ I^- gives (84%) **6a** in aqueous KOH at ca. 100 °C. In this study, however, only a minor amount of **6a** came from **2a** (see Experimental Section); presumably, the majority derived from **4a**. Thus, the 14% of **2a** fairly represents the maximum amount of initial $^-$OH attack at C.

(5) (a) Hudson, R. F. "Structure and Mechanism in Organo-Phosphorus Chemistry"; Academic Press: New York, 1965; pp 206–210. (b) Hands, A. R.; Mercer, A. J. H. *J. Chem. Soc.* **1965**, 6055.

(6) Bunton, C. A. *Catal. Rev.—Sci. Eng.* **1979**, *20*, 1 and references therein.

(7) Bunton, C. A.; Hong, Y. S.; Romsted, L. S. In "Solution Behavior of Surfactants"; Mittal, K. L., Fendler, E. J., Eds.; Plenum Press: New York, 1982; Vol. 2, p 1137. An adaptation of eq 7 was used. Several calculations were made for [**1b**] = 0.001 M with K_{OH}^{Br} values of 12–21 (those given for hexadecyltrimethylammonium bromide) and β values of 0.6–0.9. It was also assumed that the density of micellar **1b** is 1 and that the Stern layer constitutes half of its volume. The CMC assumed for **1b** was that determined for **2b**.[2]

(8) Micellar catalysis would also be expected, but reaction kinetics were not studied.

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