SYNTHESIS OF β-BONDED DIMERS – 1,10,15,20-TETRAPHENYLPORPHYRIN DERIVATIVES

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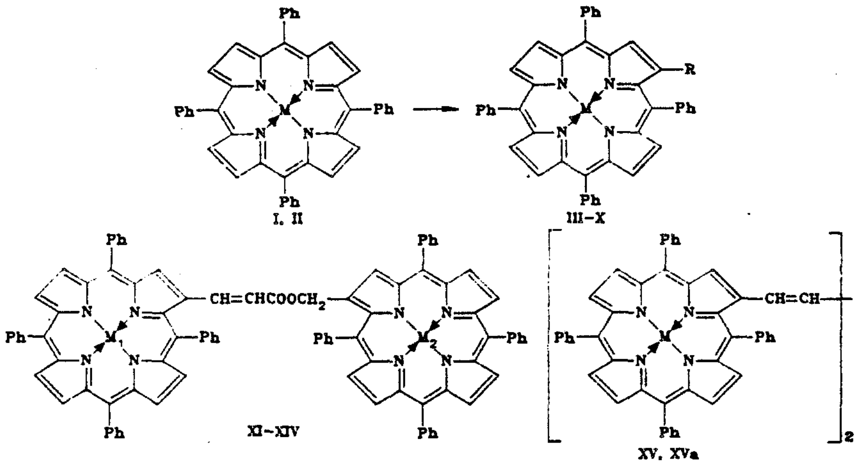
The synthesis of dimers in which the macrocycles are connected by an ester bond was accomplished starting from tetraphenylporphyrin. Dimers containing the metal in one and two porphyrin rings were obtained. It is shown that exclusively the E isomer of 1-(2-carboxyvinyl)-5,10,15,20-tetraphenylporphyrin is formed in the decarboxylation of 1-(2,2-dicarboxyvinyl)-5,10,15,20-tetraphenylporphyrin.

Covalently bonded bisporphyrins and their metal complexes have recently been the subject of intensive study [1]. Diverse derivatives of dimeric compounds of metalloporphyrins have been synthesized in order to create efficient photocatalysts [2, 3], as well as to study photosynthesis [4]. 5,10,15,20-Tetraphenylporphyrin (TPP) is most often used for these purposes because of its accessibility. Syntheses of bisporphyrins on the basis of TPP, in which connection of the macrocycles occurs at one of the aryl groups, have been described [5-7]. We have synthesized dimers of TPP that are connected by an ester bond at the β positions of the porphyrin ring.

Hydroxy and carboxy derivatives of TPP were obtained for the synthesis of the bisporphyrins. 2-Formyl-5,10,15,20-tetraphenylporphyrin (III) was synthesized by a known method [8] from prophyrin I, while copper complex (IV) was synthesized from porphyrin (II) [9]. The formyl groups of derivatives III and IV were reduced with sodium borohydride to hydroxymethyl groups with the production of 2-hydroxymethyl-5,10,15,20-tetraphenylporphyrin V and its copper complex VI, respectively.



$VI + IX \longrightarrow XI$; $VI + X \longrightarrow XII$;

$XII + Zn^{2+} \longrightarrow XIII$; $XI + Zn^{2+} \longrightarrow XIV$

I M=Co, II, IV, VI, VII, VIIa M=Cu; III, V, VIII, VIIIa, IX, X, XV $M=H_2$; III, IV R=CHO; VII, VIII $R=CH=C(COOCH_3)_2$; VIIa, VIIIa $R=CH=C(COOH)_2$; IX R=CH=CHCOOH; X R=CH=CHCOCl; XI $M_1=M_2=H_2$; XII $M_1=H_2$, $M_2=Cu$; XIII $M_1=Zn$, $M_2=Cu$; XIV $M_1=M_2=Zn$; XVa M=Zn

We used the Knoevenagel reaction in the synthesis of the carboxy component [9]. The copper complex (VII) of 1-[2,2-bis(methoxycarbonyl)vinyl]-5,10,15,20-tetraphenylporphyrin was obtained in 63% yield in the reaction of IV with dimethyl malonate. The copper was removed from complex VII by passing hydrogen chloride into a mixture of dichloroethane and

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methanol (10:1) in the presence of catalytic amounts of trifluoroacetic acid; the yield of 1-[2,2-bis(methoxycarbonyl)vinyl]-5,10,15,20-tetraphenylporphyrin (VIII) was 93%. Absorption bands corresponding to the stretching vibrations of an ester carbonyl group (1732 cm^{-1}) and a conjugated double bond (1615 cm^{-1}) are present in the IR spectrum of VIII. Compounds VII and VIII were very stable, and we were unable to remove one of the carbomethoxy groups by pyrolysis in pyridine. To obtain IX we carried out a similar Knoevenagel reaction, but with malonic acid in this case. The very high polarity of the copper complex (VIIa) of 2-(2,2-dicarboxyvinyl)-5,10,15,20-tetraphenylporphyrin made it possible to use, for its isolation, chromatography without prior workup of the reaction mass and also made it possible to reuse the unchanged formyl derivative IV.

Because of the low solubility of VIIa in organic solvents, the copper was removed from it by the method in [10] in order to prove the structure. The yield of 2-(2,2-dicarboxyvinyl)-5,10,15,20-tetraphenylporphyrin (VIIIa) was 50% based on IV. It should be noted that the IR spectrum of VIIIa contains absorption bands corresponding to the stretching vibrations of a carboxy C=O group (1705 cm^{-1}) and an ionized carboxy group (1678 cm^{-1}).

The decarboxylation of porphyrin VIIIa was carried out by refluxing in pyridine in the presence of lithium fluoride. 2-(2-Carboxyvinyl)-5,10,15,20-tetraphenylporphyrin (IX) was obtained in 69% yield after workup of the reaction mixture and chromatography on silica gel. According to the PMR spectral data, the spin-spin coupling constant (SSCC) of the protons of the substituted vinyl group is 15.5 Hz; this is in good agreement with the data in [8] for the E isomer of the methyl ester of porphyrin IX (15.5 Hz).

The methyl ester of porphyrin IX was previously synthesized [7, 8] on the basis of formylporphyrin III and its copper complex IV by the Wittig reaction in the form of a mixture of the E and Z isomers. Exclusively the E isomer of porphyrin IX is formed in our case. By chromatography of the products of the decarboxylation of porphyrin VIIIa we isolated a compound (4% yield), to which bisporphyrin XV structure with conjugated macrocycles was assigned on the basis of data from the IR, electronic, and PMR spectra. The IR spectrum of bisporphyrin XV does not contain absorption bands corresponding to the stretching vibrations of carbonyl groups but does contain absorption bands that are characteristic for conjugated double bonds. The electronic spectrum contains two Soret bands (437 and 472 nm), and in the visible region the absorption maximum of one of the four bands has a value of 701 nm. According to the data in [11], conjugated bisporphyrins have absorption bands at 700-750 nm. The PMR spectrum also confirms the presence of conjugated double bonds.

Zinc complex XVa was obtained by treatment of dimer XV with a saturated solution of zinc acetate in methanol.

To construct the ester bond in the synthesis of the dimers we selected O-acelation with the use of an acid chloride. Treatment of porphyrin IX with oxalyl chloride gave acid chloride X, which was stable and was isolated and characterized completely. The absorption band at 1775 cm^{-1} in the IR spectrum of this compound corresponds to the stretching vibrations of the carbonyl group in acid chlorides.

Dimer XI was synthesized by the reaction of acid chloride X in refluxing dichloroethane or pyridine with porphyrin V for 2 h in the presence of 4-N,N-dimethylaminopyridine. The dimer was isolated by preparative TLC on silica gel, and the yield was 21%. The electronic spectrum of dimer XI contains two Soret bands, which correspond to the Soret bands of the monomers that make up the dimer — 419 nm (V) and 436 nm (IX). The PMR spectrum of dimer XI is the sum of the PMR spectra of porphyrins V and IX, from which it was synthesized. For definitive proof of the structure of dimer XI we carried out its alkaline hydrolysis in a mixture of dioxane and an 80% solution of potassium hydroxide in 80% ethanol. After workup of the reaction and chromatography on silica gel we obtained only two reactions products, viz., porphyrins V and IX; this was established by chromatographic comparison of the reaction products with standard monomers, as well as by comparison of their electronic spectra with the spectra of starting porphyrins V and IX, which coincided completely.

Zinc complex XIV was obtained in 91% yield by treatment of dimer XI with zinc acetate in methanol. The electronic spectrum of this compound contains two Soret bands (424 and 434 nm). The PMR spectrum of zinc complex XIV is the sum of the spectra of the monomers that make up the dimer.

To obtain dimers with different metals we synthesized dimer XII, which contains a copper atom in only one porphyrin macrocycle. The condensation of acid chloride X with copper complex VI was carried out in pyridine by heating to 85°C in the presence of 4-N,N-dimethylaminopyridine. Compound XII was isolated by preparative TLC on silica gel. The yield of dimer XII was 25%. The Soret band in the electronic spectrum of this compound is asymmetrical, since the Soret bands of the monomers that make up the dimer have markedly different molar extinction coefficients: 416 nm (log ε 5.65) for complex VI, and 436 nm (log ε 5.32) for porphyrin IX. The visible region of the electronic spectrum of dimer XII is the sum of the spectra of the monomers that make up the dimer.

Copper-zinc complex XIII was obtained in 82% yield by treatment of dimer XII with zinc acetate in methanol. The mild conditions used for introduction of zinc into dimer XII could not lead to disruption of the dimeric structure, and the electronic spectrum, which is the sum of the electronic spectra of the monomers, is therefore good evidence for the structure of mixed dimer XIII.

EXPERIMENTAL

The individuality of the compounds obtained was monitored by TLC [DC-Alufolien Kieselgel 60F254 (Merck)] in the following systems: chloroform (A), chloroform—methanol (9:1) (B), and benzene (c). The IR spectra were recorded with a Shimadzu IP-435 spectrometer. The electronic spectra were obtained with a Shimadzu UV-240 spectrophotometer. The PMR spectra were recorded with a Bruker WM-250 spectrometer (250 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The mass spectra were recorded with a Hitachi spectrometer by the method of bombardment with fast atoms.

2-Hydroxymethyl-5,10,15,20-tetraphenylporphyrin Copper Complex (VI). A 200-mg sample of sodium borohydride was added to a solution of 100 mg of copper complex IV in a mixture of 100 ml of chloroform and 10 ml of methanol, after which the reaction mass was stirred at 20°C for 30 min. It was then washed with water (three 150-ml portions) and passed through a layer (2 by 3 cm) of aluminum oxide (neutral, activity II). The solvent was removed in vacuo, and the residue was crystallized from chloroform—methanol to give 81 mg (80%) of a product with R_f 0.27 (A). UV spectrum ($CHCl_3$), λ_{max} (log ε): 416 (5.65), 572 sh (3.48), 536 (4.35), and 547 nm (3.60). IR spectrum (mineral oil): 3620 cm^{-1} (OH). Mass spectrum, m/z (%): 706 (M^+, 100), 688 (20). Found: C 76.0; H 4.4; N 8.0%. $C_{45}H_{30}CuN_4O$. Calculated: C 76.5; H 4.3; N 7.9%.

2-Hydroxymethyl-5,10,15,20-tetraphenylporphyrin (V). This compound was obtained by the method in [7] from porphyrin III and had R_f 0.39 (A). UV spectrum (benzene), λ_{max} (log ε): 419 (5.52), 480 sh (3.62), 515 (4.24), 547 (3.82), 593 (3.69), and 652 nm (3.50). IR spectrum (mineral oil): 3543 (OH), 3300 cm^{-1} (NH). Mass spectrum, m/z (%): 645 (M^+, 100), 627 (10).

1-[2,2-Bis(methoxycarbonyl)vinyl]-5,10,15,20-tetraphenylporphyrin Copper Complex (VII). A 168-mg (0.239 mmole) sample of copper complex VI, 0.5 ml of dimethyl malonate, and 0.5 ml of piperidine were added to 5 ml of pyridine, and the reaction mass was maintained at 90-100°C for 6 h. The solvent was removed in vacuo, and the residue was introduced into a column (2.5 by 25 cm) packed with silica gel L 100 × 250 and eluted with benzene. The fraction with R_f 0.35 (B) was collected, the solvent was removed in vacuo, and the residue was crystallized from methylene chloride—ethanol to give 124 mg (63%) of a product with R_f 0.35 (B). UV spectrum (benzene), λ_{max} (log ε): 428 (5.42), 548 (4.29), and 588 nm (3.89). IR spectrum (CH_2Cl_2): 1735 cm^{-1} (ester CO). Found: C 72.8; H 4.7; N 6.8%. $C_{50}H_{34}CuN_4O_4$. Calculated: C 73.4; H 4.2; N 6.8%.

1-[2,2-Bis(methoxycarbonyl)vinyl]-5,10,15,20-tetraphenylporphyrin (VIII). Hydrogen chloride was passed for 30 min with stirring at 20°C through a solution of 170 mg (0.208 mmole) of copper complex VII in a mixture of 50 ml of dichloroethane, 5 ml of methanol, and 1 ml of trifluoroacetic acid, after which the reaction mass was washed successively with 250 ml of 2 N potassium hydroxide solution and water (three 200-ml portions), dried with sodium sulfate, and passed through a layer (2 by 3 cm) of aluminum oxide (neutral, activity II). The solvent was removed in vacuo, and the residue was introduced into a column (2.5 by 15 cm) packed with silica gel L 40 × 100 and eluted with benzene. The fraction with R_f 0.31 (B) was collected, the solvent was removed in vacuo, and the residue was crystallized from methylene chloride—ethanol to give 146.2 mg (93.0%) of a product with R_f 0.31 (B). UV spectrum (benzene), λ_{max} (log ε): 430 (5.46), 523 (4.16), 550 (4.04), 596 (3.77), and 659 nm (3.46). IR spectrum (mineral oil): 3310 (NH); 1732 (ester CO); 1705, 1615 cm^{-1} (conjugated

–C=C–). PMR spectrum ($CDCl_3$ + 1% CF_3COOH): 8.46-8.59 (7H, m, β-H), 8.32-8.46 (10H), 7.83-8.09 (10H, all m, aromatic protons), and 7.31 ppm (1H, s, CH=C).

2-(2,2-Dicarboxyvinyl)-5,10,15,20-tetraphenylporphyrin (VIIIa). A 535-mg (0.832 mmole) sample of copper complex IV, 100 mg of malonic acid, and 5 ml of piperidine were dissolved in 150 ml pyridine, after which the reaction mass was maintained at 100°C for 1 h. It was then cooled to 20°C and passed through a layer (3 by 10 cm) of silica gel L 40 × 100. The pyridine solution that did not contain reaction products was heated again at 100°C for 1 h after prior addition of 50 mg of malonic acid. After cooling to 20°C, the reaction mass was passed for a second time through the same layer of silica gel. The reaction products were eluted from silica gel with 330 ml of chloroform–acetic acid (1:1). The solution was washed with water (three 300-ml portions), and the precipitate that formed in the chloroform layer was separated, washed with 100 ml of water, dried, and crystallized from chloroform–methanol. It was dried in a vacuum desiccator and then stirred in 15 ml of phosphorus oxychloride after adding a few drops of water. After 1 h, the reaction mass was poured into 1 liter of water, and the resulting precipitate was separated, washed with 500 ml of water, air dried, and crystallized from chloroform–methanol–hexane (3:1:2) to give 300 mg (49.5%) of a product with R_f 0.18 (B). UV spectrum ($CHCl_3$ + CF_3COOH), λ_{max} (log ε): 428 (5.28), 525 (4.24), 562 sh (3.72), 602 (3.78), and 661 nm (3.72). IR spectrum (mineral oil): 3302 (NH); 1705 (CO in COOH); 1678 (CO in COO); 1620, 1595 cm^{-1} (conjugated C=C). PMR spectrum ($CDCl_3$ + 1% D_5-pyridine): 9.0 (1H), 8.86 (2H), 8.84 (2H), 8.80 (2H, all s, β-H), 7.65-8.24 (two OH, m, aromatic protons), and 7.60 ppm (1H, d, J = 7.5 Hz, C$\underline{H}$=C). Found: C 79.3; H 4.5; N 7.9%. $C_{48}H_{32}N_4O_4$. Calculated: C 79.1; H 4.4; N 7.7%.

2-(2-Carboxyvinyl)-5,10,15,20-tetraphenylporphyrin (IX). A solution of 169 mg (0.232 mmole) of porphyrin VIIIa in 10 ml of pyridine was refluxed for 30 h in the presence of 150 mg of lithium fluoride, after which the pyridine was removed in vacuo, and the residue was dissolved in 200 ml of chloroform. The chloroform solution was washed successively with 200 ml of 1 N hydrochloric acid and water (three 250-ml portions) and dried with sodium sulfate. The solvent was removed in vacuo, and the residue was separated with a column (2.5 by 40 cm) packed with silica gel L 40 × 100 by elution with chloroform. The fraction with R_f 0.63 (B) was collected, the solvent was removed in vacuo, and the residue was crystallized from chloroform–heptane to give 110 mg (69%) of a product with R_f 0.63 (B). UV spectrum ($CHCl_3$), λ_{max} (log ε): 436 (5.31), 526 (4.22), 569 (3.83), 604 (3.76), and 663 nm (3.62). IR spectrum (mineral oil): 3300 (NH); 1679 (CO in COO^-); 1615, 1595 cm^{-1} (conjugated C=C). PMR spectrum ($CDCl_3$): 9.00 (1H), 8.85 (2H) 8.81 (2H, all s, β-H), 8.26-8.72 (two OH, m aromatic protons), 7.52 (1H, d, J = 15.5 Hz, C$\underline{H}$=CHCO), and 6.60 ppm (1H, d, J = 15.5 Hz, CH=C$\underline{H}$CO). Mass spectrum, m/z (%): 686 (M^+, 100), 669 (10), 665 (10), 641 (25). Found: C 81.9; H 4.7; N 7.8%. $C_{47}H_{32}N_4O_2$. Calculated: C 82.4; H 4.7; N 8.2%.

2-{2-[(5,10,15,20-Tetraphenyl-2-porphyryl)methoxycarbonyl]vinyl}-5,10,15,20-tetraphenylporphyrin (XI). A 42.7-mg (0.062 mmole) sample of porphyrin IX was dissolved in 1.5 ml of oxalyl chloride, and the reaction mass was stirred at 20°C for 1.5 h. The oxalyl chloride was removed in vacuo, a solution of 38.5 mg (0.06 mmole) of porphyrin VI and 40 mg of 4-N,N-dimethylaminopyridine in 50 ml of dichloroethane was added to the residue, and the reaction mass was refluxed for 2 h. The solvent was removed in vacuo, and the residue was dissolved in 100 ml of chloroform. The chloroform solution was washed successively with 150 ml of 1 N hydrochloric acid and water (three 200-ml portions). the organic layer was dried with sodium sulfate, the solvent was removed in vacuo, and the residue was introduced into a column (2 by 30 cm) packed with silica gel L 40 × 100 and eluted with benzene. The fraction with R_f 0.18 (C) was additionally separated by preparative TLC on silica gel in chloroform–hexane (1:1). The solvent was removed in vacuo, and the residue was crystallized from chloroform–methanol to give 16.2 mg (20.7%) of a product with R_f 0.18 (C). UV spectrum ($CHCl_3$), λ_{max} (log ε): 420 (5.60), 449 (5.49), 520 (4.53), 551 (4.10), 596 (4.04), and 653 nm (4.06). IR spectrum (mineral oil): 3296 (NH), 1710 cm^{-1} (ester CO). PMR spectrum ($CDCl_3$): 9.00 (1H), 8.92 (1H, all s, β-H), 8.65-8.88 (12H, m, β-H), 7.55-8.30 (4 OH, m, aromatic protons), 7.37 (1H, d, J = 16 Hz, C$\underline{H}$=CHCO), 6.62 (1H, d, J = 16 Hz, CH=C$\underline{H}$CO), and 5.73 ppm (2H, s, C$\underline{H}_2$OCO).

1,4-Bis(5,10,15,20-tetraphenyl-1-porphyrinato)-1,3-butadiene (XV). Chromatography of the products of the reaction to obtain porphyrin IX via the preceding method gave 6.8 mg (4%) of dimer XV with R_f 0.81 (B) and 0.27 (A). UV spectrum (benzene), λ_{max} (log ε): 437 (5.14), 568 (4.55), 601 (4.40), 640 (4.15), and 701 nm (4.15). IR spectrum (mineral oil):

3300 (NH); 1594.9, 1550 cm^{-1} (conjugated C=C). PMR spectrum ($CDCl_3$): 10.00 (2H), 9.83 (2H), 9.64 (2H), 9.44 (2H), 9.23 (2H), 9.03 (2H), 8.94 (2H, all d, J = 5 Hz, β-H), 7.48-8.82 (4 OH, m, aromatic protons), 7.32-7.48 (2H, m C$\underline{H}$=CH—CH=C$\underline{H}$), and 6.82-6.95 ppm (2H, m, CH=C$\underline{H}$—C$\underline{H}$=CH).

1,4-Bis(5,10,15,20-tetraphenyl-1-porphyrinato)-1,3-butadiene Zinc Complex (XVa). A 4-ml sample of a saturated solution of zinc acetate in methanol was added to a solution of 21 mg (0.016 mmole) of bisporphyrin XV in 30 ml of chloroform, after which the reaction mass was stirred for 1 h, the solvent was removed in vacuo, and the residue was dissolved in 50 ml of chloroform. The solution was passed through a layer (2 by 3 cm) of aluminum oxide (neutral, activity IV), the solvent was removed in vacuo, and the residue was crystallized from chloroform—hexane (1:3) to give 18 mg (78.0%) of a product with R_f 0.74 (B). UV spectrum (benzene), λ_{max} (log ε): 445 (5.41), 470 (5.20), 516 sh (4.89), 601 (4.44), and 662 nm (4.50). IR spectrum (mineral oil): 1655, 1594 cm^{-1} (conjugated C=C). PMR spectrum ($CDCl_3$): 10.09 (2H), 9.73 (2H); 9.41 (2H), 9.12 (2H), 8.95 (2H), 8.83 (2H), 8.71 (2H, all d, J = 5 Hz, β-H), 7.49-8.65 (4 OH, m, aromatic protons), 7.40-7.49 (2H, m, C$\underline{H}$=CH—CH=C$\underline{H}$), and 6.84-6.95 ppm (2H, m, CH=C$\underline{H}$—C$\underline{H}$=CH).

2-[2-(Chlorocarbonyl)vinyl]-5,10,15,20-tetraphenylporphyrin (X). Chromatography of the products of the reaction to obtain dimer XI via the preceding method gave the prophyrin; after crystallization from chloroform, the yield was 9.3 mg (21%) [R_f 0.75 (B)]. UV spectrum ($CHCl_3$), λ_{max} (log ε): 437 (5.26), 526 (4.27), 569 (3.90), 604 (3.82), and 663 nm (3.70). IR spectrum (mineral oil): 3300 (NH), 1775 (CO in COCl), and 1611 cm^{-1} (conjugated C=C). PMR spectrum ($CDCl_3$): 9.16 (1H, s, β-H), 8.72-8.94 (6H, m, β-H), 7.56-8.35 (2 OH, m, aromatic protons), 7.50 (1H, d, J = 15.5 Hz, C$\underline{H}$=CHCO), and 6.69 ppm (1H, d, J = 15.5 Hz, CH=C$\underline{H}$CO).

2-{2-[(5,10,15,20-Tetraphenyl-2-porphyrinyl)methoxycarbonyl]vinyl}-5,10,15,20-tetraphenylporphyrin Zinc Complex (XIV). A 2-ml sample of a saturated solution of zinc acetate in methanol was added to a solution of 9 mg (6.86 mmole) of dimer XI in 50 ml of chloroform, after which the reaction mass was stirred at 20°C for 1 h. The solvent was then removed in vacuo, and the residue was dissolved in 30 ml of chloroform. The solution was passed through a layer (2 by 3 cm) of aluminum oxide (neutral, activity II), and the solvent was removed in vacuo. The residue was crystallized from chloroform—methanol to give 9 mg (91.2%) of a product with R_f 0.52 (A). UV spectrum (benzene), λ_{max} (log ε): 424 (5.65), 434 sh (5.53), 517 sh (3.89), 553 (4.54), and 595 nm (2.0). IR spectrum (mineral oil): 1740 (ester CO). PMR spectrum ($CDCl_3$): 9.14 (1H, s), 9.02 (1H, s), 8.84-8.98 (9H, m), 8.78 (1H, d, all β-H), 7.56-8.30 (4 OH, m, aromatic protons), 7.42 (1H, d, J = 16 Hz, C$\underline{H}$=CHCO), 6.60 (1H, d, J = 16 Hz, CH=C$\underline{H}$CO), and 5.35 ppm (2H, s, C$\underline{H}_2$OCO).

2-{2-[(5,10,15,20-Tetraphenyl-2-porphyrinyl)methoxycarbonyl]vinyl}-5,10,15,20-tetraphenylporphyrin (XII). A 150.5-mg (0.219 mmole) sample of porphyrin IX was dissolved in a mixture of 10 ml of oxalyl chloride and 5 ml of dichloroethane, and the reaction mass was maintained at 20°C for 1 h. The solvent was removed in vacuo, the residue was dissolved in 100 ml of pyridine, 103.5 mg (0.147 mmole) of copper complex VI and 2 mg of 4-N,N-dimethylaminopyridine were added, and the reaction mass was maintained at 85°C for 4 h. The solvent was removed in vacuo, and the residue was separated by preparative TLC on silica gel in chloroform—hexane (1:1). The fraction with R_f 0.39 (C) was collected, the solvent was removed in vacuo, and the residue was crystallized from chloroform—methanol to give 51.5 mg (25%) of a product with R_f 0.39 (C). UV spectrum (benzene), λ_{max} (log ε): 418 (5.72), 430 sh (5.51), 538 (4.48), 600 (3.77), 647 sh (3.38), and 657 nm (3.45). IR spectrum (mineral oil): 3300 (NH), 1710 cm^{-1} (CO). Found: C 81.0; H 4.8; N 8.1%. $C_{92}H_{60}CuN_8O_2$. Calculated: C 80.5; H 4.4; N 8.2%.

2-{2-[(5,10,15,20-Tetraphenyl-2-porphyrinyl)methoxycarbonyl]vinyl}-5,10,15,20-tetraphenylporphyrin Copper Zinc Complex (XIII). A 4-ml sample of a saturated solution of zinc acetate in methanol was added to a solution of 21 mg (0.015 mmole) of dimer XII in 30 ml of chloroform, and the reaction mixture was stirred at 20°C for 1 h. The solvent was removed in vacuo, and the residue was dissolved in 50 ml of chloroform. The solution was passed through a layer (2 by 5 cm) of aluminum oxide (neutral, activity II). The solvent was removed in vacuo, and the residue was crystallized from chloroform—hexane (1:3) to give 18 mg (81.9%) of a product with R_f 0.31 (C). UV spectrum (benzene), λ_{max} (log ε): 416 (5.70), 438 (5.38), 495 (3.82), 541 (4.42), 560 sh (4.34), and 605 nm (3.94). IR spectrum (mineral oil): 1712 (CO); 1660, 1609, 1595 cm^{-1} (conjugated C=C).

Hydrolysis of Dimer XI. A solution of 3 mg ($2.3 \cdot 10^{-3}$ mmole) of dimer XI in a mixture of dioxane and 2 N KOH in 80% ethanol was maintained at 20°C for 18 h, after which it was extracted with chloroform (three 30-ml portions). The extract was washed successively with 50 ml of 0.2 N hydrochloric acid and water (three 100-ml portions) and dried with sodium sulfate. The solvent was removed in vacuo, and the residue was separated by preparative TLC on silica gel L 5 × 40 in chloroform—hexane (5:1). The first fraction (V) was collected to give 1 mg (34%) of a product with R_f 0.39 (A). UV spectrum (benzene), λ_{max}: 419, 480, 515, 547, 593, and 552 nm. The second fraction (IX) was collected to give 1 mg (32%) of a product with R_f 0.63 (B). UV spectrum ($CHCl_3$), λ_{max}: 436, 526, 604, and 663 nm.

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REACTIONS OF INDOLES WITH POLYFLUOROCARBONYL COMPOUNDS

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Indoles with different substituents in the 1- and 2-positions of the indole ring react with hexafluoroacetone and methyl trifluoropyruvate to give the 3-alkylated derivatives. The compounds obtained show high fungicidal activity in plants.

Indole (Ia) is known to react [1, 2] with hexafluoroacetone (II) in ether or toluene to give 3-(α-hydroxyhexafluoroisopropyl)indole (IIIa). This reaction is the only example of the C-alkylation of indoles by polyfluorocarbonyl coompounds. We here present some further results of a study of the C-alkylation of indole and 2-methyl, 2-phenyl, and 1-methyl-2-phenylindoles (Ib-d) with hexafluoroacetone (II) and methyl trifluoropyruvate (IV).

The 2-substituted indoles (Ib, c) and the 1,2-disubstituted indole (Id) react with the ketone (II) as readily as indole (Ia) itself. For example, the indole (IIIb) is obtained in chloroform with spontaneous heating of a mixture of 2-methylindole (Ib) and the ketone (II) from —60 to 20°C. Under similar conditions, indoles (Ic, d) react with (II) to give the 3-(α-hydroxyhexafluoroisopropyl)indoles (IIIc, d). All the products were obtained in near-quantitative yields (Table 1).

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*Deceased.

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