opening by phosphide at the less substituted position. In fact, the cyclic intermediate 8 was also present when 7 was generated, as evidenced by the spectral data. Besides signals due to the aromatic protons and methyl protons of 8 in the ^{1}H NMR, two sets of doublet of doublet absorptions at δ 4.19 (dd, J = 7.5 Hz, J_{PNCH} = 3.6 Hz, 2 H) and δ 3.67 (dd, J = 7.5 Hz, J_{PNCH} = 2.6 Hz, 2 H), for H and H′, respectively, clearly indicate the formation of the four-membered ring. The downfield shift in the ^{31}P NMR (38.1 ppm) indicates that the phosphorus is being deshielded by the positive charge on the imino salt.

In summary, the use of iminophosphorane as a protecting group for a primary amine function results in a practical, efficient procedure for the preparation of amino-containing phosphines.

Experimental Section

All of the reactions, manipulations, and purification steps involving phosphines were performed under a nitrogen atmosphere. Compounds 4, 10, and 11 were prepared according to methods described previously.[5,8,9]

2-(Azidomethyl)-2-methyl-1,3-propanediol Isopropyl Acetal (5). A mixture of compound 4 (37.71 g, 120 mmol), NaN_3 (23.41 g, 360 mmol) and water (20 mL) in DMF (200 mL) was heated with an oil bath at 100 °C for 40 h. The reaction mixture was poured into water (400 mL) and extracted with ether (100 mL × 3). The organic extracts were combined, dried, and concentrated. The residue was chromatographed on silica (100 g) with elution of ethyl acetate/hexane (1:4). The eluate was collected and concentrated to give 5 as colorless liquid (17.05 g, 75%): ^{1}H NMR δ 3.52 (s, 4 H), 3.42 (s, 2 H), 1.36 (s, 3 H), 1.33 (s, 3 H), 0.76 (s, 3 H).

Anal. Calcd for $C_8H_{15}O_2N_3$: C, 51.88; H, 8.16; N, 22.69. Found: C, 51.84; H, 8.25; N, 23.12.

2,2-Bis[(methanesulfonyloxy)methyl]-1-azidopropane (6). A mixture of compound 5 (2.13 g, 11.4 mmol), water (2 mL), THF (10 mL), and a few drops of HCl was heated to reflux for 1 h. Concentration of the mixture provided a colorless liquid which solidified to yield a white solid (1.65 g). This material was dissolved in a solution of triethylamine (4.5 mL) in dichloromethane (50 mL) with stirring at ice-cooled temperature. Methanesulfonyl chloride (2.66 g, 23.2 mmol) was added dropwise to the above solution. The resulting mixture was allowed to warm to room temperature with stirring for another 2 h. A solution of 2% NaOH solution was added, and the organic layer was separated. The organic portion was washed with 10% HCl (30 mL) and saturated $NaHCO_3$ (30 mL). The solution was then dried in concentrated to give the desired product as a light-yellow viscous liquid (3.14 g, 92%): ^{1}H NMR δ 4.09 (s, 4 H), 3.42 (s, 2 H), 3.09 (s, 6 H), 1.10 (s, 3 H).

Anal. Calcd for $C_7H_{15}N_3O_6S_2$: C, 27.90; H, 5.02; N, 13.94. Found: C, 27.56; H, 5.28; N, 14.33.

2,2-Bis[(diphenylphosphino)methyl]-1-aminopropane (1). A solution of triphenylphosphine (3.49 g, 13.3 mmol) in THF (20 mL) was added to a solution of compound 6 (4.0 g, 13.3 mmol) in THF (50 mL), and the resulting solution was allowed to stir at room temperature for 24 h. Diphenylphosphide anion was prepared by treating diphenylphosphine (5.4 g, 29.0 mmol) in THF (100 mL) with a 1.6 M hexane solution of n-BuLi (20.5 mL, 32.8 mmol). The anion solution was added to the above iminophosphorane solution at 0 °C, and the resulting mixture was heated to reflux for 4 h. Degassed water (10 mL) was added, and the solution was refluxed for another 10 h. All solvents were removed by rotary evaporator, and the residue was chromatographed on silica (80 g) with elution of ethyl acetate. The eluate was collected and concentrated to give the desired produce as a clear colorless liquid which solidified to yield white solid (3.07 g, 51%): mp 57–59 °C; IR (neat) 3385, 3319 cm^{-1} (-NH_2); ^{1}H NMR δ 7.50–7.26 (m, 20 H), 2.65 (s, 2 H), 2.40–2.25 (m, 4 H), 1.00 (br, 2 H, -NH_2), 0.95 (s, 3 H); ^{13}C NMR δ 139.6 (d, J = 13 Hz), 132.8 (d, J = 21 Hz), 131.9 (d, J = 11 Hz), 128.3 (d, J = Hz), 51.7 (t, J = 9 Hz), 39.9 (m), 39.4 (m), 25.6 (t, J = 9 Hz); ^{31}P NMR δ -25.1.

Anal. Calcd for $C_{29}H_{32}NP_2$: C, 76.47; H, 6.86; N, 3.07. Found: C, 76.21; H, 6.52; N, 2.79.

Instead of the addition of water to the reaction mixture, THF solvent was removed and chloroform was added to the residue. The insoluble material was filtered off, and hexane was added to the filtrate to precipitate compound 9, which was very sensitive to water and identified by its spectral data: ^{1}H NMR δ 7.80–7.15 (m, 35 H), 3.12 (d, J_{PNCH} = 13.3 Hz, 2 H), 2.55 (dd, J_{HCH} = 14.2 Hz, J_{PCH} = 3.1 Hz, 2 H), 2.44 (dd, J_{HCH} = 14.2 Hz, J_{PCH} = 3.8 Hz, 2 H), 0.95 (s, 3 H); ^{13}C NMR (aliphatic) δ 55.8 (dt, J = 9, 5 Hz), 40.6 (m), 39.8 (m), 25.8 (t, J = 10 Hz); ^{31}P NMR δ -23.85 (-PPh$_2$), 7.5 (-N=PPh$_3$); FABMS (M + 1) 716.29.

(3-Aminopropyl)diphenylphosphine (2). A solution of triphenylphosphine (6.7 g, 25.6 mmol) in benzene (50 mL) was added to a solution of 3-chloropropyl azide (10) (3.0 g, 25.1 mmol) in benzene (50 mL) and stirred overnight. The benzene solvent was replaced with THF (100 mL). Diphenylphosphide anion was prepared by addition of a 1.60 M hexane solution of n-butyllithium to a solution of diphenylphosphine (5.2 g, 28.0 mmol) in THF and was added to the above solution. The resulting mixture was stirred at room temperature for 4 h. Water (10 mL) was then added, and the resulting mixture was heated to reflux overnight. All solvents were removed, and the residue was extracted with hexane (50 mL × 2). The extracts were dried, concentrated and distilled to give compound 2 as a colorless liquid (3.5 g, 58%): bp 136–138 °C (0.10 mmHg); ^{31}P NMR δ -15.6 (lit.[6] ^{31}P NMR δ -16.5).

(2-Aminopropyl)diphenylphosphine (3). Compound 3 was prepared from 11 in 56% yield by a method similar to that described for 1: by 140–142 °C (0.15 mmHg); IR 3362, 3287 cm^{-1}; ^{1}H NMR δ 7.50–7.25 (m, 10 H), 3.10–2.90 (m, 1 H), 2.30–2.05 (m, 2 H), 1.44 (br, 2 H), 1.19 (dd, J_{HCCH} = 6.4 Hz, J_{PCCCH} = 1 Hz, 3 H); ^{13}C NMR δ 139 (d, J = 13 Hz), 133.9 (d, J = 11 Hz), 132.5 (d, J = 19 Hz), 128.4 (d, J = 6 H), 44.9 (d, J = 15 Hz), 40.1 (d, J = 13 Hz), 25.5 (d, J = 8 Hz); ^{31}P NMR δ -21.4.

Anal. Calcd for $C_{15}H_{18}NP$ C, 74.05; H, 7.46; N, 5.76. Found: C, 74.39; H, 7.08; N, 5.41.

Acknowledgment. Financial support by the National Science Council (NSC81-0208-M002-44) of the Republic of China is gratefully acknowledged.

(8) Hassner, A.; Galle, J. E. *J. Org. Chem.* **1976**, *41*, 2273.
(9) Boyer, J. H.; Hamer, J. *J. Am. Chem. Soc.* **1955**, *77*, 951.

A New Synthesis of Porphyrin Systems by Four Sequential [3 + 2] Cycloadditions of an Alkyne with Azaallenyl Radical Cations†

Felix Müller, Anke Karwe, and Jochen Mattay*

Organisch-Chemisches Institut der Universität Münster, Orléansring 23, DW-4400 Münster, Federal Republic of Germany

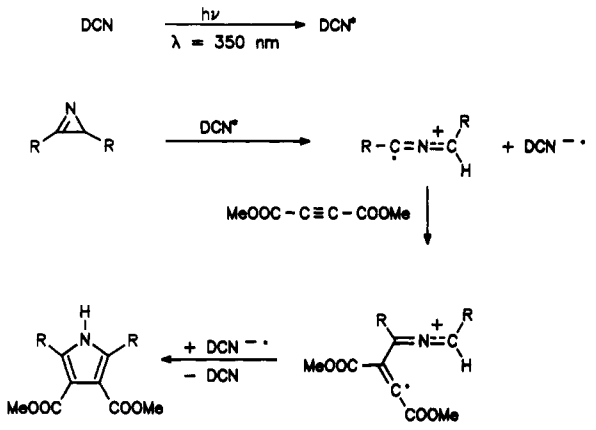
Received March 30, 1992

Porphyrins are among the main synthetic targets of organic chemistry.[1] In addition, they are of current interest as physiological active compounds[2] and as complex ligands for catalytic reactions.[3] Their spectroscopic behavior has been investigated extensively.[4] Most synthetic approaches proceed by way of a quaternary pyrrole derivative,[5] and nowadays a biomimetic pathway is preferred.[6] In this paper, we report that a porphyrin system can be built up by four consecutive [3 + 2] cycloadditions between a cyclododecane functionalized with four azirine units and an acceptor-substituted ethyne derivative under conditions of photoinduced electron transfer (PET).

† Radical Ions and Photochemical Charge-Transfer Phenomena (Series A), Part 35, and Cycloadditions (Series B), Part 39. Series A, Part 34: Heidbreder, A.; Mattay, J. *Tetrahedron Lett.* **1992**, *33*, 1973. Series B, Part 38: Köbbing, St.; Mattay, J. *Tetrahedron Lett.* **1992**, *33*, 927.

0022-3263/92/1957-6080$03.00/0

Scheme I



The 1,3-dipolar cycloaddition of azirines with acetylenes to yield pyrroles is a long-known reaction.[7] In order to allow for easy ring opening, it is crucial to have an aryl substituent which shifts the n-π^* bond to about 280 nm, next to the azirine ring. In order to open azirine rings containing aliphatic substituents, we developed a process that is controlled not by direct irradiation but by an electron transfer. According to the PET-oxidative path,[8] an electron acceptor such as 1,4-naphthalenedicarbonitrile (DCN) is irradiated with light of 350-nm wavelength. The excited DCN reacts on contact with the azirine, which accepts an electron to yield a highly reactive azirine radical cation. Ring opening of the azirine radical cation gives a linear-shaped 2-azaallenyl radical cation, which readily reacts in a two-step process[9] with a double or triple bond (Scheme I).

Because of its higher reactivity, compared to the ylide, the 2-azaallenyl radical cation adds to imines and olefins to yield imidazoles and pyrrolidines. But the main advantage of the PET reaction is that it is possible to use azirines with aliphatic substituents as starting materials. By using bicyclic azirines we were able to synthesize imidazolophanes and pyrrolophanes.[10] This prompted us to study the reaction of a pentacyclic azirine containing a cyclododecane core so as to produce, via a porphyrinogen, a porphyrin system.

As there is no easy synthesis of a 1,4,7,10-cyclododecatetraene,[11] the standard azirine preparation via the vinyl azide could not be used.[12] Instead, we prepared 1,4,7,10-cyclododecanetetrone from [2,2](2,5)furanophane according to literature procedures.[13] The tetraketone was transformed by the classic Neber process[14] into 4,8,12,16-tetraazapentacyclo[13.1.0^{3,5}.0^{7,9}.0^{11,13}.0]hexadeca-(1)16,4,8,12-tetraene (1).[15] Compound 1, dimethyl 2-butynedioate, and the DCN catalyst were irradiated in CH_3CN for 60 h in a rayonet photochemical reactor fitted with 350-nm tubes. At the end of this period, the amorphous solid that had separated from the reaction solution proved to be porphyrin 1,2,3,4,5,6,7,8-octamethyl ester 5 (Scheme II).

Proposed intermediates 2, 3, and 4 could be detected only by GC–MS coupling in very poor yield (1–2%). Recrystallization from methanol/chloroform gave a 6% yield of pure porphyrin 5 as red crystals. Compound 5 shows the characteristic features of porphyrins: a Soret band at 409 nm (log ϵ = 4.916) and methine protons shifted to δ 10.78 ppm in the ^{1}H NMR. There was no trace of the intermediate porphyrinogen.

The reaction conditions result in a quantitative transformation to the stabilized planar porphyrin. For the reaction to succeed, an electron-withdrawing substituent on the acetylenic compound is important. Compounds with electron-rich substituents, such as bis(trimethylsilyl)acetylene or 4-octyne, did not prove a porphyrin system, nor did methyl 2-butynoate.

The results described above show that a novel [3 + 2] cycloaddition of azaallenyl radical cations is a versatile and powerful method for constructing a wide range of heterocycles. Additional applications are being investigated and will be reported in due course.

Experimental Section

4,8,12,16-Tetraazapentacyclo[13.1.0^{3,5}.0^{7,9}.0^{11,13}.0]hexadeca-1(16),4,8,12-tetraene (1). A solution of hydroxylamine (0.05 mol) in 50 mL of ethanol was added to a 0 °C solution of 1,4,7,10-cyclododecanetetrone (2.16 g, 0.01 mol) in 20 mL of ethanol. After 1 h, the cooling bath was removed, and stirring was continued overnight. The solvent was evaporated, and the oxime was dissolved in diethyl ether and washed with water. After removal of the ether, the oxime was dissolved in 50 mL of pyridine, and *p*-toluenesulfonyl chloride (8.51 g, 0.05 mol) was added at ambient temperature. After 16 h, 50 mL of water was added, and azirine 1 was removed by addition of diethyl ether. Compound 1 crystallized from ether in 54% yield. 1: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.45 (d, 8 H, ^3J = 6.8 Hz, CH_2), 2.91 (t, 4 H, ^3J = 6.8 Hz, CH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 25.44 (CH_2), 30.98 (CH), 154.06 (C=N); MS (70 eV) *m/z* 212 (M^+, 0.7), 198 (1), 170 (41), 156 (38), 107 (24), 91 (100); IR (KBr) ν (cm^{-1}) 2950, 1770, 1545, 1165, 1005; UV (CH_3CN) λ_{max} (nm) (log ϵ) 235 (3.65); brown needles, mp 128 °C (uncorr). Anal. $C_{12}H_{12}N_4$ (212.2536) Calcd: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.70; H, 5.84; N, 26.75.

Porphyrin 1,2,3,4,5,6,7,8-Octamethyl Ester (5). A solution of the azirine (424 mg, 2 mmol) and dimethyl 2-butynedioate (4 mL, 28 mmol) in 50 mL of acetonitrile was poured into five Pyrex

(1) (a) Franck, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 343–352. (b) Dolphin, D., Ed. *The Porphyrins*; Academic Press: New York, 1978. (c) Johnson, A. W. *Chem. Soc. Rev.* **1975**, *4*, 1–26.

(2) De Matteis, F.; Aldridge, W. N. *Heme and Hemoproteins*; Springer: Berlin, 1978.

(3) (a) Resch, U.; Fox, M. A. *J. Phys. Chem.* **1991**, *95*, 6169–6178. (b) Ibid. **1991**, *95*, 6316–6332. (c) Weber, L.; Haufe, G.; Rehorek, D.; Hennig, H. *J. Chem. Soc., Chem. Commun.* **1991**, 502–505.

(4) (a) Scheer, H.; Katz, J. J. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 399–524. (b) Smith, K. M. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 1–28.

(5) (a) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476–482. (b) Paine, J. B. III; Kirshner, W. B.; Moskowitz, D. W.; Dolphin, D. *J. Org. Chem.* **1976**, *41*, 3857–3860. (c) Medforth, C. J.; Smith, K. M. *Tetrahedron Lett.* **1990**, *31*, 5583–5586.

(6) Franck, B.; Bringmann, G.; Wegner, Ch.; Spiegel, U. *Liebigs Ann. Chem.* **1980**, 263–274.

(7) (a) Padwa, A. In *Synthetic Organic Photochemistry*; Horspool, W., Ed.; Plenum Press: New York, 1984; pp 313–374. (b) Huisgen, R. In *1,3 Dipolar Chemistry*; Padwa, A., Ed.; John Wiley and Sons: New York, 1984; Vol. I, pp 1–176.

(8) (a) Fox, M. A.; Chanon, M., Eds. *Photoinduced Electron Transfer*; Elsevier: Amsterdam, 1988. (b) Mattay, J. *Synthesis* **1989**, 233–252. (c) Mattay, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 825–845.

(9) Müller, F.; Mattay, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1336–1337.

(10) Müller, F.; Mattay, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 207–208.

(11) Gubernator, K.; Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 686–687.

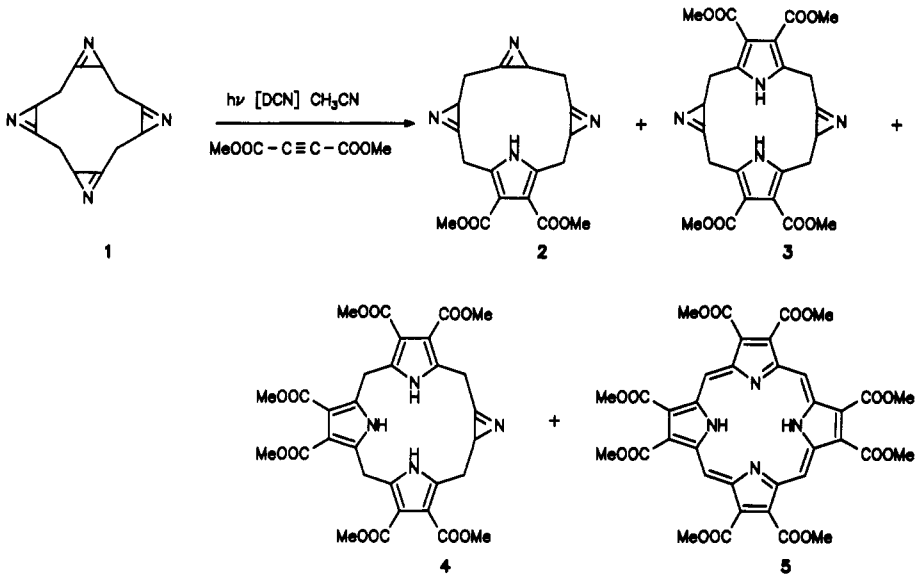
(12) (a) Smolinsky, G. *J. Org. Chem.* **1962**, *27*, 3557–3559. (b) Fowler, F. W.; Hassner, A.; Levy, L. A. *J. Am. Chem. Soc.* **1967**, *89*, 2077–2082.

(13) (a) Winberg, H. E.; Fawcett, F. S.; Mochel, W. E.; Theobald, C. W. *J. Am. Chem. Soc.* **1960**, *82*, 1428–1435. (b) Holdren, R. F.; Hixon, R. M. *J. Am. Chem. Soc.* **1946**, *68*, 1198–1200.

(14) (a) Neber, P. W.; Burgard, A. *Liebigs Ann. Chem.* **1932**, *493*, 281–294. (b) Cram, D. J.; Hatch, M. J. *J. Am. Chem. Soc.* **1953**, *75*, 33–38. (c) Ibid. **1953**, *74*, 38–44.

(15) Because of its ^{1}H and ^{13}C NMR data and the fact that the position of the C–N double bonds is derived from the starting compound, we assume that 1 has the symmetrical structure shown in Scheme II.

Scheme II



tubes. 1,4-Naphthalenedicarbonitrile (0.5 mmol, 90 mg) was added, the reaction solution was deoxygenated by argon bubbling, and the tube was sealed. Irradiation was carried out by means of a Rayonet photochemical reactor and 350-nm radiation lamps. Irradiation was maintained for 60 h. The residue was isolated and recrystallized from methanol/chloroform, 1:1. **5**: ^{1}H NMR (300 MHz, $CDCl_3$) δ -3.40 (s, 2 H, NH), 3.58 (s, 24 H, OCH_3), 10.78 (s, 4 H, CH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 53.30 (OCH_3), 107.61 (CH), 136.94 (C3), 139.10 (C2), 152.03 (C=O); MS (70 eV) m/z 774 (M^+, 1.5), 745 (2), 605 (3), 387 (15), 203 (66), 118 (100); IR (KBr) ν (cm^{-1}) 3420, 2980, 1725, 1440, 1235, 1036; UV (CH_3OH) λ_{max} (nm) (log ϵ) 491 (3.641), 409 (4.916), 332 (4.410), 205 (5.335); red-brown needles, mp 294 °C. Anal. $C_{36}H_{30}N_4O_{16}$ (774.6550) Calcd: C, 55.82; H, 3.90; N, 7.23. Found: C, 55.61; H, 3.98; N, 6.95.

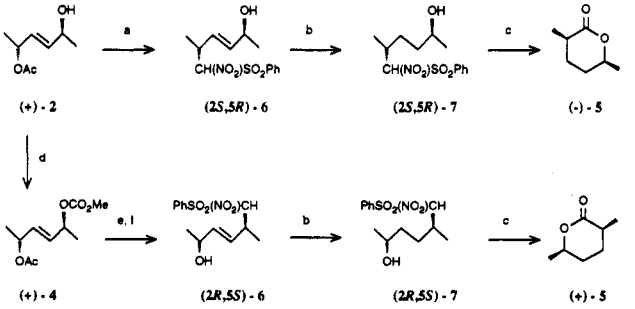
Acknowledgment. Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Bayer AG, Philips Bildröhrenwerke AG, and Heraeus (Original Hanau) AG for gifts of material and equipment. F.M. thanks the Studienstiftung des deutschen Volkes for a predoctoral grant.

Additions and Corrections

Vol. 57, 1992

Hans E. Schink and Jan-E. Bäckvall*. Synthesis of (+)-(*E*)-(2*S*,5*R*)-5-Acetoxy-3-Hexen-2-ol via Enantioselective Enzymatic Hydrolysis. An Enantiodivergent Palladium-Catalyzed Route to (+)- and (−)-*cis*-2-Methyl-5-hexanolide.

Page 1589, Scheme III. The drawings for (−)-**5** and (+)-**5** were inadvertently switched. The corrected scheme is shown below.



Takako Nakamura, Haruo Matsuyama,* Nobumasa Kamigata, and Masahiko Iyoda. Synthesis of Macrocyclic Dilactones by Cyclization of Sulfonium Salts.

Page 3788, column 1. The compounds described in paragraphs 2–6 should have *R* stereochemistry at the 3- and 5-positions.