slow (k_s) and a fast (k_f) reacting component.[22] Remarkably, the isomerization was found to be slower in 1-butanol than in the gels. Furthermore, isomerization in the (*S*)-**1** gel was found to be slower than in the (*R*)-**1** gel, especially for the fast reacting component. Apparently, the azobenzene groups in (*R*)-**2** experience a more exposed "solvent-like" environment in the (*S*)-**1** gel than in the (*R*)-**1** gel (Scheme 2). These results support the CD measurements, and can be explained by the different packing of **2** in aggregates of the same or opposite configuration leading to a difference in the free volume and polarity experienced by the azobenzene groups (Scheme 2).

Received: July 18, 2000
Revised: November 6, 2000 [Z15483]

[1] *Comprehensive Asymmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfalz, H. Yamamoto), Springer, Berlin, **1999**.
[2] E. L. Eliel, S. H. Wilen, *Stereochemistry of Organic Compounds*, Wiley, New York, **1994**.
[3] Chiral supramolecular structures: a) M. C. Feiters, R. J. M. Nolte in *Advances in Supramolecular Chemistry*, *Vol. 6* (Ed.: G. W. Gokel), JAI Press, Stamford, **2000**, p. 41, and references therein; monolayers: b) M. V. Stewart, E. M. Arnett, *Topics in Stereochemistry*, *Vol. 13*, Wiley, New York, **1982**, p. 220; c) E. M. Arnett, N. G. Harvey, P. L. Rose, *Acc. Chem. Res.* **1989**, *22*, 131; liquid crystals: d) F. Stevens, D. J. Dyer, D. M. Walba, *Angew. Chem.* **1996**, *108*, 955; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 900; e) Y. Takanishi, H. Takezoe, Y. Suzuki, I. Kobayashi, T. Yajima, M. Terada, K. Mikami, *Angew. Chem.* **1999**, *111*, 2502; *Angew. Chem. Int. Ed.* **1999**, *38*, 2353.
[4] Discrete complexes: a) C. D. Tran, J. H. Fendler, *J. Am. Chem. Soc.* **1980**, *102*, 2923; b) A. Dobashi, N. Saito, Y. Motoyama, S. Hara, *J. Am. Chem. Soc.* **1986**, *108*, 307; c) S. K. Ghosh, *J. Peptide Res.* **1999**, *53*, 261; d) G. Castronuovo, V. Elia, A. Pierro, F. Velleca, *Can. J. Chem.* **1999**, *77*, 1218; e) S. Hanessian, R. Saladino, R. Margarita, M. Simard, *Chem. Eur. J.* **1999**, *5*, 2169; f) M. Asakawa, H. M. Janssen, E. W. Meijer, D. Pasini, J. F. Stoddart, *Eur. J. Org. Chem.* **1998**, 983.
[5] Micellar aggregates: reviews: a) A. Dobashi, M. Hamada, *J. Chromatogr. A* **1997**, *780*, 179; b) H. Wan, L. G. Blomberg, *J. Chromatogr. A* **2000**, *875*, 43; see, for example: c) J. Bella, S. Borocci, G. Mancini, *Langmuir* **1999**, *15*, 8025.
[6] Self-assemblies in organic solvents: a) M. T. Cung, M. Marraud, J. Neel, *Biopolymers* **1978**, *17*, 1149; b) B. S. Jursic, S. I. Goldberg, *J. Org. Chem.* **1992**, *57*, 7172.
[7] a) P. Terech, R. G. Weiss, *Chem. Rev.* **1997**, *97*, 3133; b) J. van Esch, F. S. Schoonbeek, M. de Loos, E. M. Veen, R. M. Kellogg, B. L. Feringa, *NATO ASI Ser. Ser. C* **1999**, *527*, 233–259; c) J. H. van Esch, B. L. Feringa, *Angew. Chem.* **2000**, *112*, 2351; *Angew. Chem. Int. Ed.* **2000**, *39*, 2263.
[8] a) R. Oda, I. Huc, S. J. Candau, *Angew. Chem.* **1998**, *110*, 2838; *Angew. Chem. Int. Ed.* **1998**, *37*, 2689; b) D. J. Abdallah, L. Lu, R. G. Weiss, *Chem. Mater.* **1999**, *11*, 2907; c) C. Shi, Z. Huang, S. Kilic, J. Xu, R. M. Enick, E. J. Beckman, A. J. Carr, R. E. Melendez, A. D. Hamilton, *Science* **1999**, *286*, 1540; d) L. A. Cuccia, J.-M. Lehn, J.-C. Homo, M. Schmutz, *Angew. Chem.* **2000**, *112*, 239; *Angew. Chem. Int. Ed.* **2000**, *39*, 233; e) U. Beginn, G. Zipp, A. Mourran, P. Walther, M. Möller, *Adv. Mater.* **2000**, *12*, 513.
[9] K. Hanabusa, K. Shimura, K. Hirose, M. Kimura, H. Shirai, *Chem. Lett.* **1996**, 885.
[10] a) J. van Esch, S. De Feyter, R. M. Kellogg, F. De Schryver, B. L. Feringa, *Chem. Eur. J.* **1997**, *3*, 1238; b) J. van Esch, F. Schoonbeek, M. de Loos, H. Kooijman, A. L. Spek, R. M. Kellogg, B. L. Feringa, *Chem. Eur. J.* **1999**, *5*, 937.
[11] Bis-ureas (*R*)-**1**, (*S*)-**1**, (*R*)-**2**, and (*S*)-**2** were prepared by adding the corresponding isocyanate to (*R*,*R*)- or (*S*,*S*)-1,2-diaminocyclohexane. Bis-urea **1** gelates solvents such as *p*-xylene, chloroform, cyclohexane, and butanol; see ref. [10b]. Compound **2** is poorly soluble in solvents such as butanol and *p*-xylene ($c \leq 2$ mM) but gels chloroform and benzene thermoreversibly ($c \leq 4$ mM).
[12] Measurements were performed at 50 °C, which is above the gel–sol phase transition.
[13] J.-L. Dimicoli, C. Hélène, *J. Am. Chem. Soc.* **1973**, *95*, 1063.
[14] J. Jadzyn, M. Stockhausen, B. Zywucki, *J. Phys. Chem.* **1987**, *91*, 754.
[15] M. Akiyama, T. Ohtani, *Spectrochim. Acta Part A* **1994**, *50*, 325.
[16] Explanation of the symbols: A = host (*R*)-**1** or (*S*)-**1**; D = guest (*R*)-**2**; c = total urea concentration (M); δ_a = chemical shift of the fully aggregated state; δ_{obs} = observed chemical shift; δ_m = chemical shift of the monomer.
[17] FT-IR measurements on **2** ($CHCl_3$; 2 mM) showed a shift of the NH stretch and amide I band from 3435 and 1663 cm^{-1} for a solution at approximately 50 °C (monomer) to 3322 and 1628 cm^{-1} for a gel at 20 °C (hydrogen-bonded aggregates), see Y. Mido, *Spectrochim. Acta Part A* **1973**, *29*, 431. ^{1}H NMR titration experiments of **2** ($CDCl_3$; 2–0.5 mM) revealed just a slight change (less than 0.006 ppm).
[18] It was assumed that as **1** and **2** exhibit the same bis(ureido)cyclohexane skeleton the effect of aggregation on the chemical shift of the NH1 proton of **2** is similar when **2** is incorporated in stacks of **1** as in stacks of pure **2**. It is then possible to treat the chemical shift of **2** (δ_{obs}) as a function of the total concentration (c) of (*R*)-**2** + **1**, and Equation (1) can be applied. Self-association of **2** is negligible at $c \leq 2$ mM.
[19] X. Song, J. Perlstein, D. G. Whitten, *J. Am. Chem. Soc.* **1997**, *119*, 9144.
[20] N. Harada, K. Nakanishi, *Circular Dichroic Spectroscopy*, University Science Books, Mill Valley, **1983**.
[21] *Photochromism, Molecules and Systems* (Eds.: H. Dürr, H. Bouas, H. Laurent), Elsevier, Amsterdam, **1990**.
[22] C. Ruslim, K. Ichimura, *Macromolecules* **1999**, *32*, 4254.

Palladium-Catalyzed Domino Reaction of 4-Methoxycarbonyloxy-2-butyn-1-ols with Phenols: A Novel Synthetic Method for Cyclic Carbonates with Recycling of CO_2**

Masahiro Yoshida and Masataka Ihara*

Allylic and propargylic carbonates are well-known compounds that undergo a variety of palladium-catalyzed transformations, which make up an important class of palladium-catalyzed reactions.[1, 2] The key step in these reactions is the formation of a π-allyl- or -allenylpalladium complex by facile decarboxylation, which undergoes a variety of further transformations under neutral conditions. In these reactions, CO_2 is produced as a co-product in the decarboxylation step, but there are few reports on the recycling of this CO_2 molecule.[3] Recently, the chemistry of CO_2 has received much attention from the viewpoint of carbon resources and environmental problems,[4] and the fixation of CO_2 as cyclic carbonates represents an attractive area of organic synthesis.[5–9] Here we report a novel synthesis of cyclic carbonates by palladium-catalyzed domino reaction of 4-methoxycarbonyloxy-2-butyn-

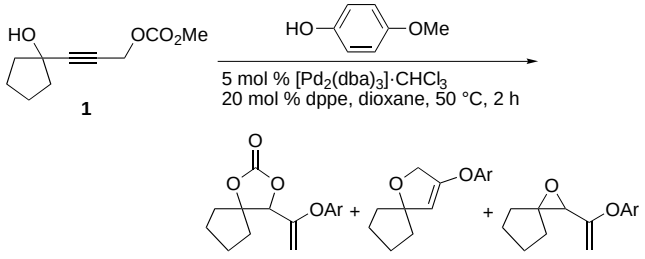
[*] Prof. M. Ihara, M. Yoshida
Department of Organic Chemistry
Graduate School of Pharmaceutical Sciences
Tohoku University, Aobayama, Sendai, 980-8578 (Japan)
Fax: (+81) 22-217-6877
E-mail: mihara@mail.pharm.tohoku.ac.jp

[**] M.Y. acknowledges support from the Research Fellowships of the Japan Society for the Promotion of Science (JSPS) for Young Scientists.

  1433-7851/01/4003-0616 $ 17.50+.50/0

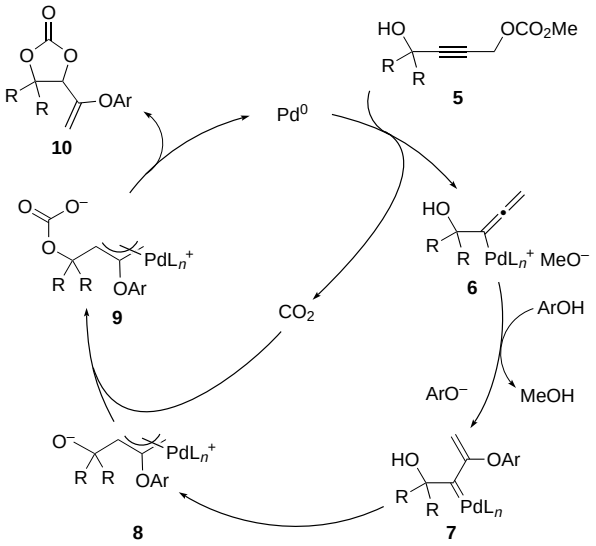
1-ols with phenols. The reaction enables the efficient construction of cyclic carbonates in a one-pot process with recycling of the CO_2 molecule.

In an initial experiment, we found that the reaction of **1** and *p*-methoxyphenol with $[Pd_2(dba)_3]\cdot CHCl_3$ and dppe under Ar in a sealed tube provided the cyclic carbonate **2a** in 85% yield with a small amount of dihydrofuran **3** and traces of epoxide **4** (Scheme 1). A plausible mechanism for the reaction is shown in Scheme 2. By reaction with palladium catalyst, the propargylic carbonate **5** would undergo elimination of CO_2 to give



	2a	3	4
under Ar (in sealed tube)	85%	5%	trace
under CO_2 (1 atm)	96%	0%	0%
bubbling Ar	21%	32%	11%

Scheme 1. Domino reactions of **1** in the presence and absence of CO_2. dba = dibenzylideneacetone, dppe = 1,2-bis(diphenylphosphanyl)ethane, Ar = *p*-methoxyphenyl.

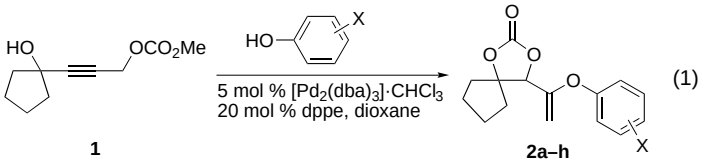


Scheme 2. Proposed reaction mechanism for the type of domino reaction shown in Scheme 1.

the allenylpalladium methoxide **6**, which would be subject to nucleophilic attack by phenols to give the π-allylpalladium complex **8** via the intermediate **7**. Finally, **8** would re-fix CO_2 to afford the carbonate species **9**, which would subsequently cyclize to produce the aryloxy-substituted cyclic carbonate **10**. It is expected that by-products **3** and **4** would be produced by direct cyclization of π-allylpalladium complex **8**.[10] To the best of our knowledge, this is the first example of efficient re-fixation of the CO_2 molecule from a decarboxylation reaction. To confirm this, we examined the reactions in the presence and absence of CO_2 (Scheme 1). When the reaction was carried out in a CO_2 atmosphere, the yield of **2a** increased to 96%. In contrast, when the reaction was carried out under bubbling Ar to remove the resulting CO_2, only 21% yield of **2a** was obtained together with 32% yield of **3** and 11% yield of **4**. These results provide strong evidence that decarboxylation is followed by re-fixation of the CO_2 molecule in the reaction cycle.

To examine the scope of this reaction, we next attempted the reaction of **1** with various substituted phenols ArOH [Eq. (1), Table 1]. All of the reactions successfully proceeded

Table 1. Domino reactions of **1** with various substituted phenols [Eq. (1)].



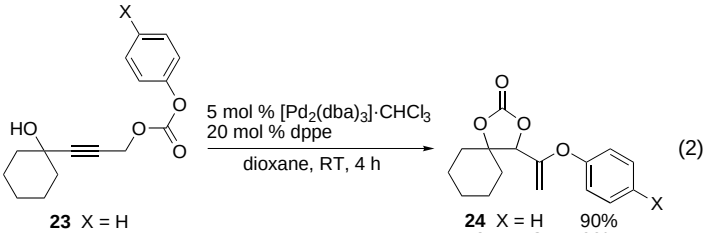
(1)

Entry	X	*T* [°C]	*t* [h]	Product	Yield [%]
1	4-OMe	50	2	**2a**	85
2	2-OMe	RT	3	**2b**	90
3	4-Me	RT	5	**2c**	87
4	H	RT	9	**2d**	81
5	[a]	RT	4	**2e**	74
6	4-Cl	50	2	**2f**	70
7	4-F	50	2	**2g**	54
8	4-acetyl	50	5	**2h**	36

[a] ArOH = 1-naphthol.

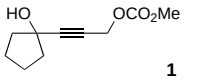
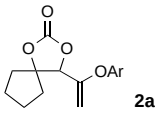
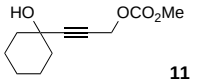
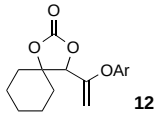
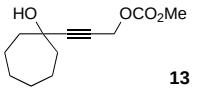
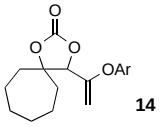
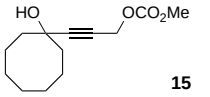
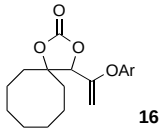
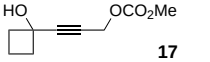
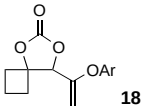
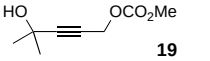
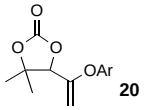
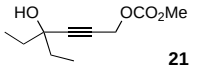
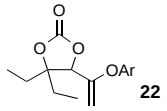
to give the corresponding cyclic carbonates **2a–h** in moderate to good yields. In particular, the products were produced in high yields when **1** was treated with phenols bearing electron-donating substituents (entries 1–3). Some results of palladium-catalyzed domino reactions of various propargylic carbonates with *p*-methoxyphenol are summarized in Table 2. The reactions of **1**, **11**, **13**, and **15**, which contain five- to eight-membered rings, with *p*-methoxyphenol provided the corresponding cyclic carbonates in high yields (entries 1–4). Interestingly, **17**, which is known to be transformed into the aryloxy-substituted cyclopentanone at high temperature,[11] was converted into the cyclic carbonate **18** in 63% yield at room temperature (entry 5). The reactions of acyclic substrates **19** and **21** also gave the corresponding products **20** and **22** (entries 6 and 7). Although the yield of **22** was not high (42%), it dramatically increased to 97% when the reaction was carried out under an atmosphere of CO_2 (entry 7).

The reaction was applicable to 4-aryloxycarbonyloxy-2-butyn-1-ols **23** and **25**, in which the nucleophilic phenolic components were present within the molecule [Eq. (2)]. The



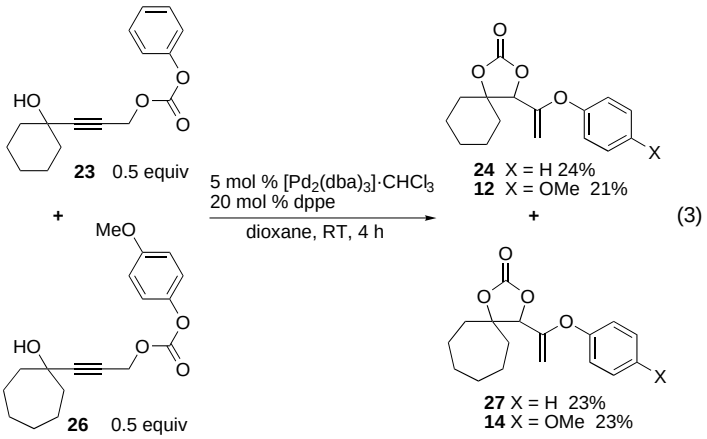
(2)

Table 2. Domino reactions of various propargylic carbonates with *p*-methoxyphenol.[a]

Entry	Substrate	T [°C]	Product[b]	Yield [%][c]
1	 **1**	50	 **2a**	85 (96)
2	 **11**	RT	 **12**	91
3	 **13**	RT	 **14**	89
4	 **15**	RT	 **16**	80
5	 **17**	RT	 **18**	63
6	 **19**	50	 **20**	83
7	 **21**	50	 **22**	42 (97)

[a] Reactions were carried out in the presence of 5 mol% $[Pd_2(dba)_3]\cdot CHCl_3$, 20 mol% dppe, and 1.1 equiv of *p*-methoxyphenol in dioxane under argon for 2–5 h. [b] R = *p*-methoxyphenyl. [c] The yields in parentheses are for reactions carried out under CO_2 (1 atm).

reactions of **23** and **25** with the palladium catalyst gave the desired cyclic carbonates **24** and **12**. Compound **12** was obtained almost quantitatively. A crossover experiment showed that the aryloxide ion was completely dissociated from the propargyl unit in the reaction [Eq. (3)]. This implies



(3)

that the reaction proceeds through the degradation of propargylic carbonates into three components—allenylpalladium species, aryloxide, and CO_2—followed by re-formation of these components with high efficiency.

In conclusion, we have developed a novel synthesis of cyclic carbonates by palladium-catalyzed domino reactions of 4-methoxycarbonyloxy-2-butyn-1-ols with phenols. The reaction enables the construction of cyclic carbonates by efficient re-fixation of the CO_2 molecule under mild conditions, which is a very convenient and environmentally friendly method. The utility of this reaction in organic synthesis and its application to catalytic asymmetric reactions are now under investigation.

Experimental Section

General procedure for the palladium-catalyzed domino reaction of 4-methoxycarbonyloxy-2-butyn-1-ols with phenols: Reaction of **11** with *p*-methoxyphenol (Table 2, entry 2): *p*-Methoxyphenol (26.9 mg, 0.217 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (10.2 mg, 0.0099 mmol), and dppe (15.7 mg, 0.0394 mmol) were added to a stirred solution of **11** (41.8 mg, 0.197 mmol) in dioxane (3 mL) at room temperature. After being stirred for 4 h at room temperature, the reaction mixture was concentrated, and the residue was purified by chromatography on silica gel with hexane/AcOEt (90/10) as eluant to give **12** (54.9 mg, 91%) as colorless needles. M.p. 80–83 °C; IR (KBr): $\tilde{\nu}$ = 2925, 2850, 1795, 1620 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.18–1.40 (m, 1H), 1.61–1.85 (m, 7H), 1.97–2.13 (m, 2H), 3.80 (s, 3H), 4.17 (d, J = 3.0 Hz, 1H), 4.47 (d, J = 3.0 Hz, 1H), 4.72 (s, 1H), 6.86–6.92 (m, 2H), 6.95–7.01 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.8, 21.9, 24.6, 30.6, 36.6, 55.5, 83.1, 85.6, 89.7, 114.9 (2C), 122.1 (2C), 147.1, 153.9, 156.3, 157.0; MS (70 eV): *m*/*z* 304 [M^+]; HR-MS calcd for $C_{17}H_{20}O_5$ 304.1311; found 304.1314.

Received: September 26, 2000
Revised: October 31, 2000 [Z15856]

[1] a) J. Tsuji, I. Minami, *Acc. Chem. Res.* **1987**, *20*, 140; b) J. Tsuji, *Tetrahedron* **1986**, *42*, 4361, and references therein.
[2] J. Tsuji, T. Mandai, *Angew. Chem.* **1995**, *107*, 2830; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2589, and references therein.
[3] Bäckvall et al. reported that the palladium-catalyzed reaction of an allylic carbonate in the presence of an amine led to allylic carbamates as complicated by-products. The reaction proceeds by nucleophilic attack on the π-allylpalladium intermediate by R_2NCOO^-, which is generated in situ from CO_2 and amine. J. E. Bäckvall, K. L. Granberg, A. Heumann, *Isr. J. Chem.* **1991**, *31*, 17.
[4] a) E. Haruki, T. Ito, A. Yamamoto, N. Yamazaki, F. Higashi, S. Inoue in *Organic and Bio-organic Chemistry of Carbon Dioxide* (Eds.: S. Inoue, N. Yamazaki), Kodansha, Tokyo, **1981**; b) W. Keim, *NATO ASI Ser. Ser. C* **1987**, *206*, 23; c) M. M. Halmann, *Chemical Fixation of Carbon Dioxide*, CRC Press, Boca Raton, **1993**.
[5] For the reactions of oxiranes, see: A. Behr, *Carbon Dioxide Activation by Metal Complexes*, VCH, Weinheim, **1988**, p. 91.
[6] For the reactions of propargylic alcohols, see: a) K. Iritani, N. Yanagihara, K. Utimoto, *J. Org. Chem.* **1986**, *51*, 5499; b) Y. Inoue, K. Ohuchi, S. Imaizumi, *Tetrahedron Lett.* **1988**, *29*, 5941; c) Y. Inoue, J. Ishikawa, M. Taniguchi, H. Hashimoto, *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1204; d) Y. Sasaki, P. H. Dixneuf, *J. Org. Chem.* **1987**, *52*, 4389; e) J. Fournier, C. Bruneau, P. H. Dixneuf, *Tetrahedron Lett.* **1989**, *30*, 3981.
[7] For Pd^0-catalyzed reactions of vinyl epoxides, see: a) T. Fujinami, T. Suzuki, M. Kamiya, S. Fukuzawa, S. Sakai, *Chem. Lett.* **1985**, 199; b) B. M. Trost, S. R. Angle, *J. Am. Chem. Soc.* **1985**, *107*, 6123; c) B. M. Trost, J. K. Lynch, S. R. Angle, *Tetrahedron Lett.* **1987**, *28*, 375; d) S. Wershofen, H. D. Scharf, *Synthesis* **1988**, 854; e) S. Suzuki, Y. Fujita, Y. Kobayashi, F. Sato, *Tetrahedron Lett.* **1989**, *30*, 3487.

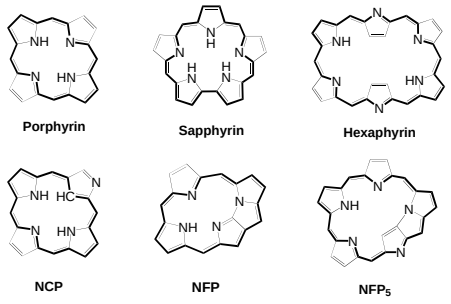
  1433-7851/01/4003-0618 $ 17.50+.50/0

[8] For Pd^0-catalyzed reactions of alkadienols with aryl halides, see: K. Uemura, D. Shiraishi, M. Noziri, Y. Inoue, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1063.
[9] For the utility of cyclic carbonates, see: a) L. Hough, J. E. Priddle, R. S. Theobald, *Adv. Carbohydr. Chem.* **1960**, *15*, 91; b) V. Amarnath, A. D. Broom, *Chem. Rev.* **1977**, *77*, 183.
[10] For similar reactions to form dihydrofurans and epoxides via π-allylpalladium complexes, see: a) S. Ma, Z. Shi, *J. Org. Chem.* **1998**, *63*, 6387; b) S. Ma, S. Zhao, *J. Am. Chem. Soc.* **1999**, *121*, 7943.
[11] M. Yoshida, H. Nemoto, M. Ihara, *Tetrahedron Lett.* **1999**, *40*, 8583.

N-Fused Pentaphyrin

Ji-Young Shin, Hiroyuki Furuta,* and Atsuhiro Osuka*

Porphyrin analogues have been attracting considerable attention not only from the interest of annulenic chemistry but also from their use in a variety of applications.[1] Recently, reinvestigation of the Rothemund-type pyrrole–aryl aldehyde condensation[2] has revealed the concurrent formation of a porphyrin isomer, the *N*-confused porphyrin (**NCP**),[3] and expanded porphyrins such as sapphyrin[4] and hexaphyrin[5].



We have also reported a new analogue, the *N*-fused porphyrin (**NFP**), in which a unique fused tri-pentacyclic ring exists in the porphyrin core as the result of an inversion of the confused ring in **NCP**.[6] Herein we report the first example of a normal-type of fused expanded porphyrin, *N*-fused pentaphyrin (**NFP_5**), which contains a fused tri-pentacyclic ring in the core.

The title compound was synthesized under similar Rothemund-type conditions, namely, the acid-catalyzed condensation of pentafluorobenzaldehyde and unsubstituted pyrrole, followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Along with the *meso*-pentafluorophenylporphyrin (12%), *meso*-pentafluorophenylhexaphyrin[5] (20%), and other higher homologues of *meso*-aryl type (around 13%),[7] yellowish (**1-Y**) and reddish (**1-R**) products, both of which show parent mass peaks in the fast atom bombardment (FAB) mass spectra corresponding to the pentapyrrolic macrocycle, could be isolated in a total yield of approximately 15%. The ratio of the two products **1-R** and **1-Y** changed greatly according to the amounts of oxidant used and converged to **1-R** when DDQ was used in excess (2.5 equiv). The similar products **2** and **3** were also obtained, in yields of 19 and 2%, respectively, from the analogous reactions with 2,6-dichloro- and 2,4,6-trimethylbenzaldehyde.[8] Although the reaction is not optimized yet, the relatively high concentration of reactants (> 50 mM) seems effective for the formation of products.

The structure of the *N*-fused product **1-Y** was revealed by X-ray analysis on a single crystal (Figure 1).[9] A fused tri-pentacyclic ring with inward- and outward-pointing nitrogen atoms was found in a pentapyrrolic core. The inner nitrogen atom N(27) of the fused ring was connected to the β-carbon atom C(3) of the neighboring pyrrole ring. One of the pyrrole rings was canted significantly: the tilting angles of each ring, clockwise from the fused ring, were 24.96, 15.32, 22.46, and 99.18° to the mean plane of the 30 core atoms. Two of the

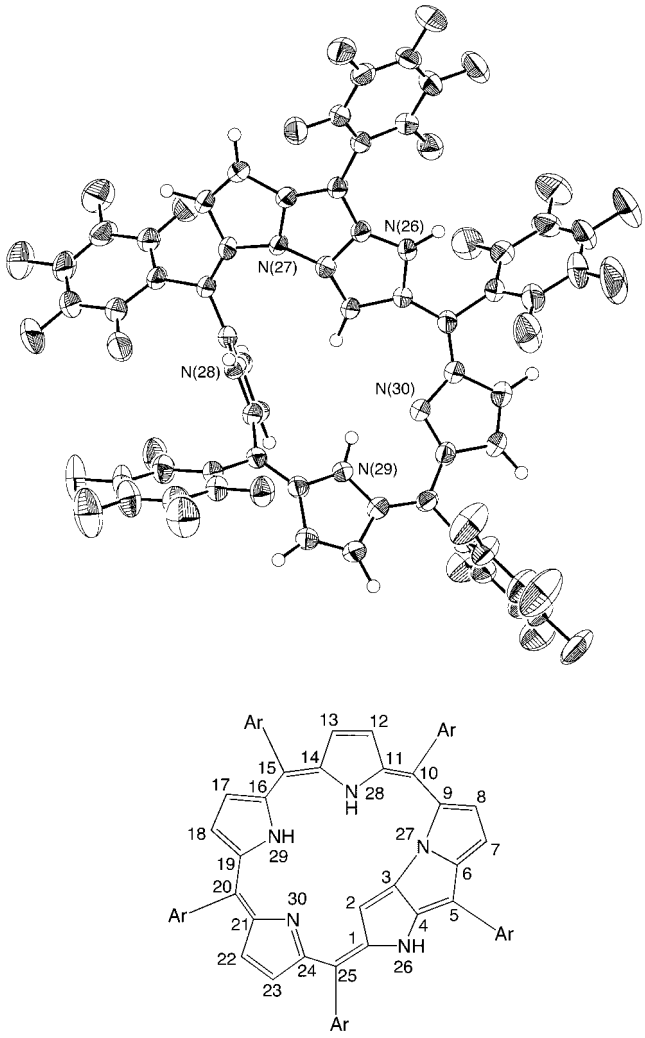


Figure 1. Top: X-ray crystal structure of *meso*-pentafluorophenyl *N*-fused pentaphyrin (**1-Y**). Bottom: Schematic representation of **NFP_5-Y** showing the numbering scheme.

[*] Prof. H. Furuta,[+] Prof. A. Osuka, J.-Y. Shin
Department of Chemistry
Graduate School of Science
Kyoto University, Kyoto 606-8502 (Japan)
Fax: (+81) 75-753-3970
[+] PRESTO, Japan Science and Technology Corporation (JST)

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

  1433-7851/01/4003-0619 $ 17.50+.50/0