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One-Pot Synthesis of Photochromic Naphthopyrans in the Solid State

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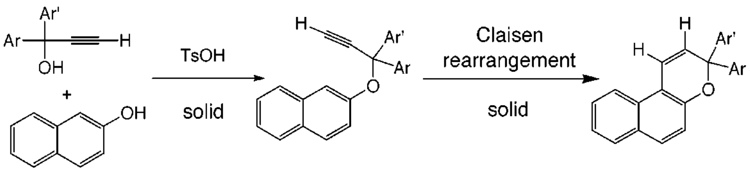
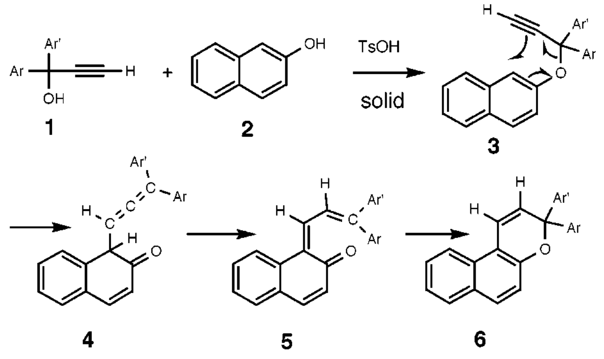
ABSTRACT



***p*-TsOH-catalyzed condensation reactions of 1,1-diaryl-2-propyn-1-ol (1) and 2-naphthol (2) in the solid state gave 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyran (6) via Claisen rearrangement. Similar reactions of 1 with 2,6- (7) and 2,7-dihydroxynaphthalenes (8) afforded naphthodipyrane derivatives 9 and 10, respectively. Bis-naphthopyran derivatives 12 were also obtained by the reaction of 1,1,6,6-tetraaryl-2,5-hexadiyn-1,6-diol (11) and 2-naphthol (2) in the solid state.**

Naphthopyran derivatives are of special interest as photochromic compounds, which have a wide variety of applications such as ophthalmic glasses, electronic display systems, optical switches, and temporary or permanent memories.[1] In continuation of our ongoing study on solvent-free organic synthesis,[2] we now wish to report a simple and efficient synthetic method for various kinds of photochromic naphthopyrans in the solid state.

A mixture of 1,1-diphenyl-2-propyn-1-ol (**1a**), 2-naphthol (**2**), *p*-TsOH (0.1 equiv), and a small amount of anhydrous silica gel as a drying agent was well ground for 10 min at room temperature using a mortar and pestle and was kept for 1 h in order to complete the reaction. The reaction mixture was chromatographed on silica gel to give 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (**6a**)[3] in 56% yield.[4] Increasing the amount of TsOH or a longer reaction time caused a decrease in the yield of **6a**, and a complex mixture of unidentified product was produced. When the reaction of **1a** and **2** was carried out in CH_2Cl_2 solution in the presence of *p*-TsOH (0.1 equiv) for 1 h, **6a** was produced in 39% yield.



a: Ar=Ar'=Ph
b: Ar=Ar'=4-methyphenyl
c: Ar=Ar'=4-chlorophenyl
d:Ar=Ph; Ar'=4-methoxyphenyl
e:Ar=Ph; Ar'=2,4-dimethyphenyl
f: Ar,Ar'=fluorenyl

This solid-state reaction involves the following two steps. First 1,1-diphenyl-2-propyn-1-ol (**1a**) and 2-naphthol (**2a**)

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(1) Gemert, B. V. In *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Guglielmetti, R. J., Eds.; Plenum Press: New York, 1999.

(2) Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025−1074.

(3) Gemert, B. V.; Bergomi, M.; Knowles, D. *Mol. Cryst. Liq. Cryst.* **1994**, *246*, 67−73.

(4) **Typical procedure.** A mixture of **1a** (0.5 g, 2.4 mmol), **2** (0.34 g, 2.4 mmol), *p*-TsOH (0.046 g, 0.24 mmol), and silica gel (1.0 g) was ground for 10 min at room temperature using a mortar and pestle, and the mixture was kept for 1 h. The reaction mixture was chromatographed on silica gel using toluene as eluent to give **6a** (0.45 g, 56% yield, mp 160−162 °C) as colorless needles.

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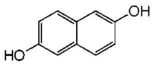
are condensed to give propargyl ether (**3a**) in the presence of *p*-TsOH. In the second step Claisen rearrangement of **3a** occurred to give **4a**, and finally naphthopynan **6a** was obtained via cyclization of quinodimethane (**5a**). Similar treatment of **1b**−**1f** with **2** gave the corresponding naphthopyrans (**6b**−**6f**) in the yields of 30−63%. (Table 1)

Table 1. One-Pot Synthesis of Naphthopyrans in the Solid State

entry	product	yield, %	mp (°C)
1	**6a**	56	160−162
2	**6b**	56	156−160
3	**6c**	30	188−192
4	**6d**	58	154−157
5	**6e**	63	122−124
6	**6f**	44	197−200

Naphthodipyran derivatives **9** and **10** were also prepared efficiently by a solid-solid reaction between **1** and 2,6- (**7**) and 2,7-dihydroxynaphthalenes (**8**). For example, when a mixture of **1a**, **7**, *p*-TsOH (0.1 equiv), and a small amount of silica gel was well ground for 10 min at room temperature in the solid state, naphthodipyran **9a** was obtained after chromatographic separation in 17% yield, which is higher than that previously reported.[5] Similarly, **9b**, **9c**, and **10a** were obtained in 13, 12, and 27% yields, respectively. When the reaction of **2** with 1,1,6,6-tetraaryl-2,5-hexadiyne-1,6-diol (**11**) was carried out, novel bis-naphthopyran derivatives **12** were obtained. For example, a mixture of **11a**, **2**, *p*-TsOH (0.1 equiv), and a small amount of silica gel was well ground for 10 min at room temperature using a mortar and pestle and was kept for 1 h. The reaction mixture was chromatographed on silica gel to give bis-naphthopyran derivative **12a** in 61% yield. Similarly, **12g** and **12f** were obtained in 41 and 57% yields, respectively. The structure of **12a** was determined by spectral data[6] and finally by X-ray crystal structure analysis (Figure 1).[7] The photochromic properties of the new bis-naphthopyran derivatives (**12**) are now under investigation.



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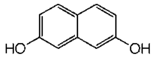

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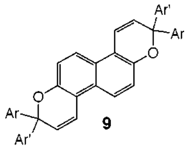

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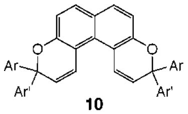

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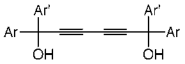

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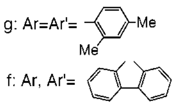
a: Ar=Ar'=Ph


g: Ar=Ar'=

f: Ar, Ar'=

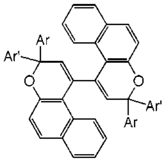


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Table 2. One-Pot Synthesis of Naphthopyrans in the Solid State

entry	product	yield, %	mp (°C)
1	**9a**	17	272−275
2	**9e**	13	231−234
3	**9f**	12	>300
4	**10a**	27	228−231
5	**12a**	61	289−291
6	**12g**	41	241−243
7	**12f**	57	297−299

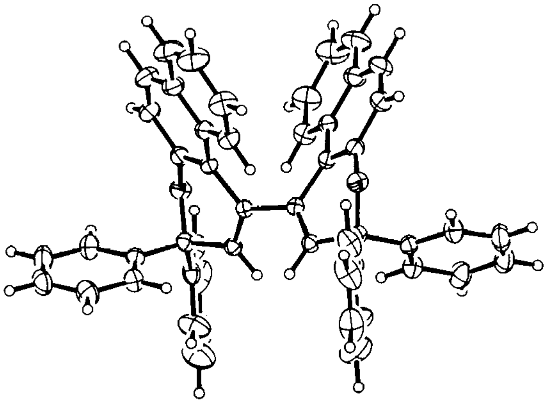

Figure 1. Ortep drawing of **12a** with 50% probability displacement ellipsoids. The molecule has a crystallographic 2-fold rotational axis. The dihedral angle between the two naphthyl rings is 56.4-(1)° and the torsion angle around the central C−C bond (C_{naph}−C−C−C_{naph}) is −44.5(5)°.

In conclusion, we have developed a simple and efficient one-pot synthesis of various kinds of photochromic naphthopyranes in the solid state. This provides an environment-friendly solventless method, avoiding the use of halogenated hydrocarbon solvents such as dichloromethane.

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(5) Knowles, D. B.; Gemert, B. V. U.S. Pat. 1995, 5,464,567.

(6) **Selected spectral data for 12a:** IR (Nujol) 1622 cm^{-1}; λ_{max} ($CHCl_3$) 242 nm (ϵ 78700), 319 nm (ϵ 7000), 356 nm (ϵ 8300); ^{1}H NMR ($CDCl_3$) δ 8.03 (d, J = 9.0 Hz, 2H), 7.70−7.06 (m, 30H), 6.15 (s, 2H); ^{13}C NMR ($CDCl_3$)δ 152.6, 144.6, 143.8, 135.9, 131.1, 130.2, 129.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 126.9, 126.5, 126.0, 123.3, 118.8, 116.8, 82.3. Anal. Calcd for $C_{50}H_{34}O_2$: C, 90.06; H, 5.14. Found: C, 90.28; H, 5.24.

(7) **X-ray Data for 12a.** $C_{50}H_{34}O_2$; M_r = 666.82; monoclinic, $C2/c$; a = 25.261(5), b = 9.112(3), and c = 17.539(3) Å, β = 115.95(1)°; V = 3630(1) Å^3; Z = 4; D_x = 1.220 g cm^{-3}; μ(Mo Kα) = 0.073 mm^{-1}; 298 K. Structure refinement with TEXSAN; all H atom parameters refined; final R = 0.044 for 2995 observed reflections. Crystallographic data (without structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143884. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax +44 1223 336033 or e-mail deposit@ccdc.cam.ac.uk).