Polish J. Chem., **78**, 361–367 (2004) **ORGANIC CHEMISTRY**

Synthesis of Naphtho[2,1-*b*]furanylium Cation and Its Reaction with Alcohols and Trialkyl Phosphites

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(Received November 17th, 2003)

The reaction between dibenzoylacetylene and 2-naphthol in the presence of a catalytic amount of pyridine leads to 2-hydroxy-1-(2-oxo-2-phenylethylidene)-2-phenyl-1,2-dihydro-naphtho[2,1-*b*]furan in nearly quantitative yield. Treatment of this heterocyclic system with trimethyl chlorosilane in chloroform leads quantitatively to 1-(2-oxo-2-phenylethylidene)-2-phenyl-1*H*-naphtho[2,1-*b*]furanylium chloride. Addition of nucleophiles such as alcohols or trialkyl phosphites to this salt produces functionalized 1,2-dihydronaphthofuran derivatives in excellent yields.

Key words: oxonium cation, naphthofuranylium cation, naphthofurans, 2-naphthol, dibenzoylacetylene

Oxygen-stabilized carbocations are important intermediates in organic chemistry [1]. Among these species α-hydroxy carbocations [2], α-alkoxy carbocations [3], acyl carbocations [4], pyrylium and benzopyrylium ions [5] have been investigated. A number of reactions have been observed which involve furanylium cations as elusive transient species [6]. In reactions in which this fully conjugated furanylium system is postulated, the cation cannot be isolated but appears to occur as an intermediate on the pathway to an observed product.

RESULTS AND DISCUSSION

Here we wish to report the synthesis and isolation of 1-(2-oxo-2-phenylethylidene)-2-phenyl-1*H*-naphtho[2,1-*b*]furanylnium chloride **2**. The reaction of 2-naphthol with dibenzoylacetylene in the presence of a catalytic amount of pyridine at ambient temperature in diethyl ether leads to 2-hydroxy-1-(2-oxo-2-phenylethylidene)-2-phenyl-1,2-dihydro-naphtho[2,1-*b*]furan **1** in nearly quantitative yield (Scheme 1).

The reaction of other "enol" systems such as 1-naphthol, acetylacetone, or 5,5-dimethyl-1,3-cyclohexandione with dibenzoylacetylene in the presence of pyridine leads to complex mixtures of products. The reaction of **1** with trimethyl chlorosilane (TMSCl) in chloroform produces **2** in quantitative yield. This salt undergoes smooth reactions with nucleophiles such as methanol, ethanol, propargyl alcohol, 1-propa-

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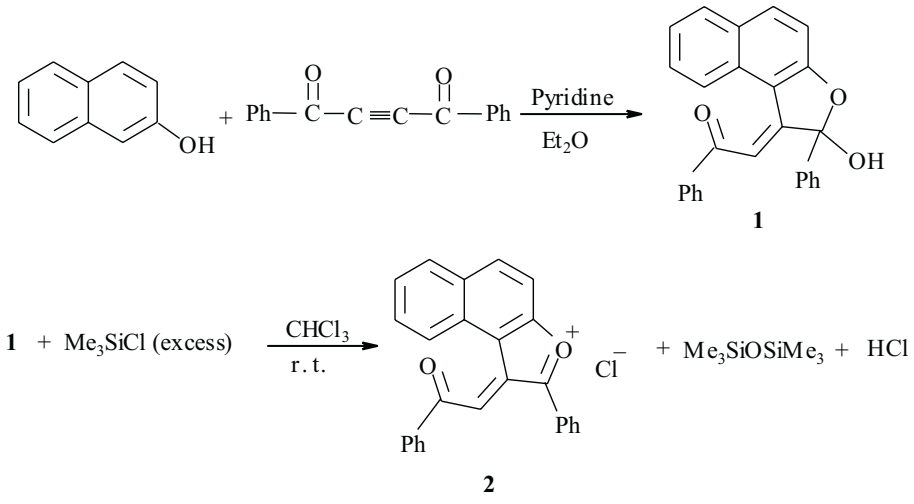
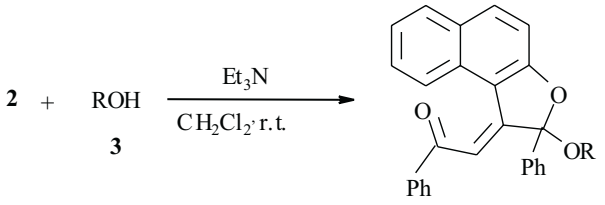
nol, or 2-propanol to produce 2-alkoxy-1-(2-oxo-2-phenylethylidene)-2-phenyl-1,2-dihydronaphtho[2,1-*b*]furans **4a–e** in excellent yields (see Scheme 2). The structures of compounds **1**, **2**, and **4a–e** were deduced from their elemental analyses and their IR, ^{1}H, ^{13}C, and ^{31}P NMR and mass spectra. The ^{1}H NMR spectrum of **1** shows a singlet (δ = 7.30) for the olefinic proton along with multiplets (δ = 7.10–8.30) for the aromatic protons. The OH proton resonance at δ = 7.50 disappeared after addition of D_2O to the $CDCl_3$ solution of **1**. The ^{1}H decoupled ^{13}C NMR spectrum of **1** exhibits 22 distinct resonances in agreement with the proposed structure.

Scheme 1



Scheme 2



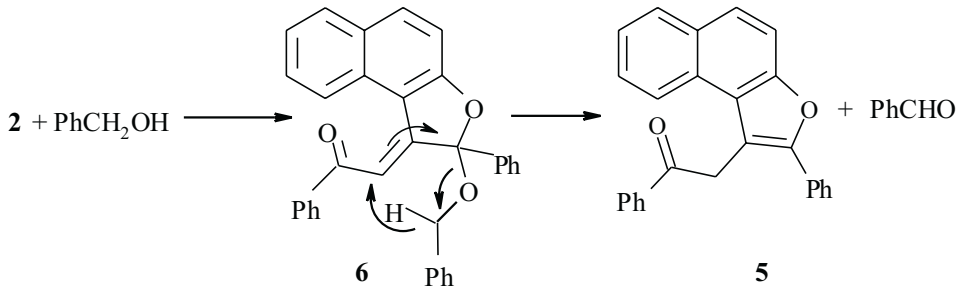
3, 4	R	Yield (%) of **4**
a	Me	94
b	Et	89
c	Propargyl	90
d	1-Propyl	92
e	2-Propyl	90

Compound **2** is a stable solid, which can be crystallized from *N,N*-dimethylformamide (DMF):TMSCl (20:1). The exposure of compound **2** to moisture causes its conversion to the starting hemi-ketal **1**. In the absence of moisture, compound **2** can be stored in the solid state at room temperature without decomposition. The ^{1}H and ^{13}C NMR spectra of **2** were measured in DMF-d_7:TMSCl (20:1) mixture. The ^{1}H NMR spectrum of **2** exhibits characteristic multiplets in the aromatic region for the phenyl and naphthyl residues. The olefinic CH of the heterocyclic system appears at δ = 9.50. The proton-decoupled ^{13}C NMR spectrum of **2** exhibits 22 distinct resonances. The carbon atom adjacent to the positively charged oxygen atom appears at δ = 171.61, which is consistent with similar oxonium structures previously reported [5c]. The olefinic methine resonance at δ = 144.30 confirms delocalization of the positive charge on this carbon atom.

The ^{1}H NMR spectrum of **4a** exhibited two singlets identified as methoxy (δ = 3.40) and olefinic (δ = 6.10) protons along with multiplets (δ = 7.10–8.61) for the aromatic protons. The proton-decoupled ^{13}C NMR spectrum of **4a** exhibits 23 distinct signals in agreement with the proposed structure. The mass spectra of compounds **4a–e** display molecular ion peaks at appropriate *m/z* values. The reaction of oxonium salt **2** with allyl or benzyl alcohol leads to known 1-phenyl-2-(2-phenylnaphtho[2,1-*b*]furan-1-yl)-1-ethanone **5** [7].

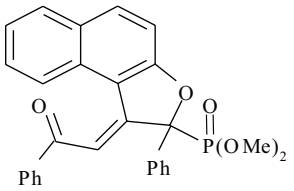
A plausible mechanism for the formation of **5** is shown in Scheme 3. The rearrangement of 2-(phenylmethoxy)-1-(2-oxo-2-phenylethylidene)-2-phenyl-1,2-dihydronaphtho[2,1-*b*]furan (**6**), produced from the addition of benzyl alcohol to **2**, leads to naphthofuran derivative **5** and benzaldehyde. The ^{1}H NMR spectrum of the reaction mixture exhibits the characteristic signals for benzaldehyde and **5** in 1:1 mole ratio.

Scheme 3

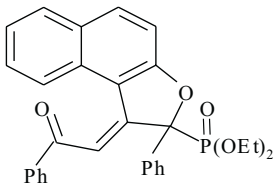


Direct additon of trimethyl phosphite to **2** in dichloromethane leads to **4f**. The ^{1}H NMR spectrum of **4f** exhibits two doublets identified as methoxy protons (δ = 3.64, 3.68) coupled with phosphorus ($^{3}J_{PH}$ = 10.5 Hz), and a doublet for the olefinic proton (δ = 6.75, $^{4}J_{PH}$ = 8.3 Hz) along with multiplets (δ = 7.10–8.61) for the aromatic moieties. The proton-decoupled ^{31}P NMR spectrum of **4f** exhibits a signal at δ = 18.70, which is attributed to the phosphoranyl group [8].

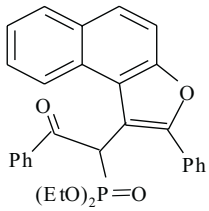
Additon of triethyl phosphite to **2** in dichloromethane leads to **4g** and **7** in 3:2 ratio. The ^{1}H NMR spectrum of **4g** exhibits a doublet for the olefinic proton (δ = 6.80, $^4J_{PH}$ = 8.7 Hz) along with multiplets (δ = 7.01–8.20) for the aromatic protons. The proton-decoupled ^{31}P NMR spectrum of **4g** exhibits a signal at δ = 19.04 for the phosphoranyl group. The ^{1}H NMR spectrum of **7** exhibits a doublet for the methine proton (δ = 5.70, $^2J_{PH}$ = 3.6 Hz) along with multiplets (δ = 7.01–8.20) for the aromatic protons. The ^{31}P NMR spectrum of **7** displays a signal at δ = 16.37 for the phosphoranyl group.



4f



4g



7

In conclusion, the reaction of 2-naphthol with dibenzoylacetylene in the presence of pyridine and subsequent treatment of the addition product with trimethylchlorosilane provides a simple entry to a fairly stable naphthofuranylium chloride derivative. Direct addition of alcohols, trimethyl phosphite, or triethyl phosphite to this salt leads to naphthofuran derivatives of potential synthetic interest.

EXPERIMENTAL

Dibenzoylacetylene was prepared by addition of ethynylmagnesium bromide to benzaldehyde [9] and subsequent oxidation [10] of the acetylenic diol. Other chemicals used in this work were purchased from Fluka (Buchs, Switzerland) and used without further purification. Melting points were measured on an Electrothermal 9100 aparatus. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer; the obtained values agreed favorably with the calculated ones. IR spectra were measured on a Shimadzu IR-460 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500.1, 125.8, and 202.4 MHz, respectively.

2-Hydroxy-1-(2-oxo-2-phenylethylidene)-2-phenyl-1,2-dihydronaphtho[2,1-*b*]furan (1). To a magnetically stirred solution of dibenzoylacetylene (0.47 g, 2 mmol) and 2-naphthol (0.29 g, 2 mmol) in Et_2O (20 mL) was added pyridine (0.016 g, 0.2 mmol) at room temperature. The reaction mixture was then stirred for 12 h. The precipitate was filtered and washed with cold diethyl ether (20 mL). The product **1** was obtained as a yellow powder. Yield 0.74 g (98%). M.p. 145–147°C. IR (KBr) (ν_{max}/cm^{-1}): 3420 (OH), 1620 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.14 (1 H, d, $^3J_{HH}$ = 8.4 Hz, CH), 7.31 (1 H, s, CH), 7.37–7.99 (14 H, m, 13 CH and OH), 8.32 (2 H, d, $^3J_{HH}$ = 7.7 Hz, H_o of COPh). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 109.95 (C), 113.34 (CH), 114.53 (C), 114.67, 122.22, 124.50, 125.54, 128.08, 128.53, 128.68, 128.91, and 129.43 (13 CH), 129.83 and 130.32 (2 C), 130.44, 133.25, and 137.95 (3 CH), 138.36, 139.92, 163.38, and 165.00 (4 C), 192.48 (C=O). MS: *m/z* (%) = 378 (M^+, 3), 273 (M^+ – COPh, 25), 105 (COPh, 100). Elemental analysis for $C_{26}H_{18}O_3$ (378.4) calcd.: C, 82.53; H, 4.79; found: C, 82.5; H, 4.8%.

1-(2-Oxo-2-phenylethylidene)-2-phenyl-1*H*-naphtho[2,1-*b*]furanylium chloride (2). To a magnetically stirred solution of **1** (0.76 g, 2 mmol) in $CHCl_3$ (20 mL)was added trimethylchlorosilane (0.43 g, 4 mmol) at room temperature. The reaction mixture was then stirred for 12 h. The precipitate was filtered and washed with $CHCl_3$ (20 mL). The product **2** was obtained as a yellow powder. Yield 0.79 g (100%). M.p. 228–230°C. IR (KBr) (ν_{max}/cm^{-1}): 1667 (C=O). ^{1}H NMR (500 MHz, DMF-d_7:TMSCl; 20:1): δ = 7.58–7.96 (8 H, m, 8 CH), 8.18 (2 H, d, $^3J_{HH}$ = 7.4 Hz, 2 CH_{ortho} of Ph), 8.21 (1 H, d, $^3J_{HH}$ = 8.4 Hz, CH), 8.43 (1 H, d, $^3J_{HH}$ = 9.3, CH), 8.77 (1 H, d, $^3J_{HH}$ = 8.4 Hz, CH), 8.83 (2 H, d, $^3J_{HH}$ = 7.1 Hz, 2 CH_{ortho} of COPh), 9.01

(1 H, d, $^3J_{HH}$ = 8.0 Hz, CH), 9.52 (1 H, s, CH); ^{13}C NMR (125.7 MHz, DMF-d_7:TMSCl; 20:1): δ = 117.23 (C), 118.83 (CH), 120.56 (C), 126.21 (CH), 126.43, 129.15, and 129.75 (3 C), 129.82, 130.22, 130.34, 130.42, 130.66, 131.11, and 131.61 (11 CH), 132.67 (C), 134.04, 136.41, 137.14, and 144.31 (4 CH), 160.85 (C), 171.58 (C=O$^+$), 194.21 (C=O). MS: *m/z* (%) = 361 (M$^+$-Cl, 5), 256 (361 – COPh, 7), 105 (COPh, 100). Elemental analysis for $C_{26}H_{17}ClO_2$ (396.9) calcd.: C, 78.68; H, 4.32; found: C, 78.7; H, 4.4%.

2-Methoxy-1-(2-oxo-2-phenylethylidene)-2-phenyl-1,2-dihydronaphtho[2,1-*b*]furan (4a). (Typical procedure). To a magnetically stirred solution of **2** (0.79 g, 2 mmol) and methanol (1 mL) in CH_2Cl_2 (20 mL) was added Et_3N (1 mL) at room temperature. The reaction mixture was then stirred for 12 h. The solvent was removed under reduced pressure, and the residue was separated by silica gel (Merck 230–400 mesh) column chromatography using *n*-hexane-ethyl acetate (4:1) mixture as eluent. Compound **4a** was obtained as a white powder. Yield 0.74 g (94%). M.p. 134–135°C, IR (KBr) (ν_{max}/cm^{-1}): 1661 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.21 (3 H, s, OMe), 6.11 (1 H, s, CH), 7.21–7.60 (10 H, m, 10 CH), 7.71 (2 H, d, $^3J_{HH}$ = 7.3 Hz, C$_o$ of Ph), 7.80 (1 H, d, $^3J_{HH}$ = 7.7 Hz, CH), 7.91 (1 H, d, $^3J_{HH}$ = 8.6 Hz, CH), 8.11 (2 H, d, $^3J_{HH}$ = 7.3 Hz, C$_o$ of Ph); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 50.74 (OMe), 99.32, and 114.24 (2 C), 118.28, 124.13, 124.93, 126.62, 126.75, 128.50, 128.61, 128.70, 128.75 and 128.84 (13 CH), 129.09 (C), 130.18 (2 CH), 130.26 (C), 131.78 and 133.80 (2 CH), 136.29, 136.42, 139.89 and 150.63 (4 C), 196.10 (C=O). MS: *m/z* (%) = 392 (M$^+$, 4), 361 (M$^+$ – OMe, 61), 256 (361 – COPh, 29), 105 (COPh, 100). Elemental analysis for $C_{27}H_{20}O_3$ (392.5) calcd.: C, 82.63; H, 5.14; found: C, 82.6; H, 5.2%.

Analogously the following compounds were obtained:

2-Ethoxy-1-(2-oxo-2-phenylethylidene)-2-phenyl-1,2-dihydronaphtho[2,1-*b*]furan (4b). Yield 89%. White powder. M.p. 126–128°C. IR (KBr) (ν_{max}/cm^{-1}): 1659 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.21 (3 H, t, $^3J_{HH}$ = 7.4 Hz, CH_3), 3.81 (2 H, m, OCH_2), 6.20 (1 H, s, CH), 7.11–8.40 (16 H, m, 16 CH); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 15.23 (CH_3), 59.13 (OCH_2), 99.26, and 113.95 (2 C), 118.24, 123.92, 124.80, 126.40, 126.58, 128.48, 128.50, 128.56, 128.61, and 128.73 (13 CH), 129.01 (C), 130.01 (2 CH), 130.06 (C), 131.53, and 133.62 (2 CH), 136.02, 136.35, 140.73, and 150.75 (4 C), 196.16 (C=O). MS: *m/z* (%) = 406 (M$^+$, 5), 361 (M$^+$ — OEt, 36), 256 (361 – COPh, 18), 105 (COPh, 100). Elemental analysis for $C_{28}H_{22}O_3$ (406.5) calcd.: C, 82.74; H, 5.46; found: C, 82.6; H, 5.5%.

2-Propargyloxy-1-(2-oxo-2-phenylethylidene)-2-phenyl-1,2-dihydronaphtho[2,1-*b*]furan (4c). Yield 90%. White powder. M.p. 135–137°C. IR (KBr) (ν_{max}/cm^{-1}): 1649 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.30 (1 H, t, $^4J_{HH}$ = 1.4 Hz, acetylenic CH), 4.21 (2 H, d, $^4J_{HH}$ = 1.4 Hz, OCH_2), 6.21 (1 H, s, CH), 7.11–8.40 (16 H, m, 16 CH); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 51.74 (OCH_2), 73.86 (C), 74.24 (CH), 99.61, and 113.35 (2 C), 118.22, 124.17, 124.86, 126.59, 126.71, 127.60, 128.31, 128.53, 128.61, and 128.93 (13 CH), 129.43 (C), 130.21 (2 CH), 130.29 (C), 131.69, and 133.79 (2 CH), 136.21, 136.38, 139.36, and 150.28 (4 C), 195.92 (C=O). MS: *m/z* (%) = 416 (M$^+$, 2), 361 (M$^+$ – OCH_2CCH, 19), 256 (361 – COPh, 32), 105 (COPh, 100). Elemental analysis for $C_{29}H_{20}O_3$ (416.5) calcd.: C, 83.63; H, 4.84; found: C, 83.7; H, 4.7%.

2-Propoxy-1-(2-oxo-2-phenylethylidene)-2-phenyl-1,2-dihydronaphtho[2,1-*b*]furan (4d). Yield 92%. White powder. M.p. 141–143°C. IR (KBr) (ν_{max}/cm^{-1}): 1658 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.78 (3 H, t, $^3J_{HH}$ = 7.3 Hz, CH_3), 1.50 (2H, m, CH_2), 3.5 (2 H, m, OCH_2), 6.1 (1 H, s, CH), 7.20–8.02 (16 H, m, 16 CH); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 10.61 (CH_3), 22.92 (CH_2), 65.06 (OCH_2), 99.20, and 113.94 (2 C), 118.35, 123.95, 124.81, 126.45, 126.62, 128.54, 128.66, 128.78, and 129.07 (13 CH), 139.06 (C), 130.11 (2 CH), 131.55 (C), 133.67 (2 CH), 136.10, 136.50, 140.84, and 150.87 (4 C), 196.28 (C=O). MS: *m/z* (%) = 420 (M$^+$, 5), 361 (M$^+$ – $OCH(CH_3)_2$, 22), 105 (COPh, 100). Elemental analysis for $C_{29}H_{24}O_3$(420.5) calcd.: C, 82.83; H, 5.75; found: C, 82.8; H, 5.7%.

2-Isopropoxy-1-(2-oxo-2-phenylethylidene)-2-phenyl-1,2-dihydronaphtho[2,1-*b*]furan (4e). Yield 90%. White powder. m.p. 140–142°C. IR (KBr) (ν_{max}/cm^{-1}): 1660 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.12 (6 H, d, $^3J_{HH}$ = 6.1 Hz, $2CH_3$), 4.05 (1 H, m, OCH), 6.10 (1 H, s, CH), 7.25–8.01 (16 H, m, 16 CH); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 15.31 ($2CH_3$), 66.90 (OCH), 99.62, and 113.51 (2 C), 118.61, 123.90, 124.90, 126.61, 126.64, 128.41, 128.50, 128.62, 128.74, 128.95 and 129.09 (13 CH), 129.5 (C), 129.99 (2 CH), 130.03 (C), 131.46, and 133.62 (2 CH), 135.95, 136.45, 141.28, and 150.86 (4 C), 196.28 (C=O). MS: *m/z* (%) = 420 (M$^+$, 5), 361 (M$^+$ – $OCH_2CH_2CH_3$, 22), 105 (COPh, 100). Elemental analysis for $C_{29}H_{24}O_3$ (420.5) calcd.: C, 82.83; H, 5.75; found: C, 82.8; H, 5.7%.

Dimethyl [1-(2-oxo-2-phenylethylidene)-2-phenyl-1,2-dihydronaphtho[2,1-*b*]furan-2-yl]-phosphonate (4f). To a magnetically stirred solution of **2** (0.79 g, 2 mmol) in CH_2Cl_2 (20 mL) was added trimethyl phosphite (0.25 g, 2 mmol) at room temperature. The reaction mixture was then stirred for 12 h. The solvent was removed under reduced pressure, and the residue was separated by silica gel (Merck 230–400 mesh) column chromatography using *n*-hexane-ethyl acetate (1:4) mixture as eluent. Compound **4f** was obtained as a white powder. Yield 0.85 g (90%). M.p. 137–140°C. IR (KBr) (ν_{max}/cm^{-1}): 1651 (C=O), 1409 (P–O). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.64, and 3.68 (6 H, 2 d, $^3J_{HP}$ = 10.5 Hz, 2 OMe), 6.77 (1 H, d, $^4J_{HP}$ = 8.3 Hz, olefinic CH), 7.12–7.57 (10 H, m, 10 CH), 7.63 (1 H, d, $^3J_{HH}$ = 7.9 Hz, CH), 7.68 (2 H, d, $^3J_{HH}$ = 7.4 Hz, 2 CH$_{ortho}$ of Ph), 7.75 (1 H, d, $^3J_{HH}$ = 8.8 Hz, CH), 7.97 (2 H, d, $^3J_{HH}$ = 7.7 Hz, 2 CH$_{ortho}$ of COPh); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 54.50, and 54.85 (2 d, $^2J_{CP}$ = 7.1 Hz, 2 OMe), 79.15 (d, $^1J_{CP}$ = 174.8 Hz, C–P), 115.11 (C), 118.35, 124.11, 124.53, and 126.72 (4 CH), 127.26 (d, $^3J_{CP}$ = 4.1 Hz, 2 CH$_{ortho}$ of Ph), 127.54 (d, $^3J_{CP}$ = 3.1 Hz, olefinic CH), 128.23 (d, $^4J_{CP}$ = 2.5 Hz, 2 CH$_{meta}$ of Ph), 128.65 (d, J_{CP} = 3.1 Hz, CH), 128.69, and 128.73 (3 CH), 128.97 (C), 129.90 (2 CH), 130.45 (C), 131.95, and 133.74 (2 CH), 136.53 (C), 136.85 (d, $^2J_{CP}$ = 10.4 Hz, C$_{ipso}$ of Ph), 136.96 (C), 151.31 (d, $^3J_{CP}$ = 14.1 Hz, C–O), 195.71 (C=O); ^{31}P NMR (202.4 MHz, $CDCl_3$): δ = 18.70 (PO_3Me_2). MS: *m/z* (%): 470 (M^+, 1), 361 (M^+ – PO_3Me_2, 30), 256 (361 – COPh, 55), 105 (COPh, 100). Elemental analysis for $C_{28}H_{23}O_5P$ (470.5) calcd.: C, 71.48; H, 4.93; found: C, 71.5; H, 4.9%.

Analogously the following compounds were obtained:

Diethyl [1-(2-oxo-2-phenylethylidene)-2-phenyl-1,2-dihydronaphtho[2,1-*b*]furan-2-1]-phosphonate (4g). Yield 60%. Yellow powder. M.p. 139–142°C. IR (KBr) (ν_{max}/cm^{-1}): 1657 (C=O), 1504 (P–O). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.19, and 1.21 (6 H, 2 t, $^3J_{HP}$ = 6.7 Hz, 2 Me), 4.38, and 3.94 (4H, m, 2OCH$_2$) 6.82 (1 H, d, $^4J_{HP}$ = 8.7 Hz, olefinic CH), 7.04–7.57 (10 H, m, 10 CH), 7.71 (1 H, d, $^3J_{HH}$ = 7.5 Hz, CH), 7.8 (2 H, d, $^3J_{HH}$ = 8.8 Hz, 2 CH$_{ortho}$ of Ph), 7.93 (1 H, d, $^3J_{HH}$ = 8.0 Hz, CH), 8.16 (2 H, d, $^3J_{HH}$ = 8.7 Hz, 2 CH$_{ortho}$ of COPh); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 16.21, and 16.63(2d, $^3J_{CP}$ = 5.6 Hz, 2Me), 63.01 and 63.51 (2d, $^2J_{CP}$ = 6.7 Hz, 2OCH$_2$), 58.42 (d, $^1J_{CP}$ = 151.64 Hz, C–P), 117.92 (C), 124.5, 124.81, 125.08, and 126.01 (4 CH), 127.32 (d, $^3J_{CP}$ = 3.8 Hz, 2 CH$_{ortho}$ of Ph), 127.91 (d, $^3J_{CP}$ = 5.6 Hz, olefinic CH), 128.51 (d, $^4J_{CP}$ = 2.8 Hz, 2 CH$_{meta}$ of Ph), 128.59, and 128.70 (3 CH), 129.51 (C), 129.62 (2 CH), 129.90 (C), 131.81, and 132.61 (2 CH), 133.70 (C), 135.74 (d, $^2J_{CP}$ = 9.2 Hz, C$_{ipso}$ of Ph), 136.62 (C), 148.90 (d, $^3J_{CP}$ = 15.09 Hz, C–O), 197.09(C=O); ^{31}P NMR (202.4 MHz, $CDCl_3$): δ = 19.04 (PO_3Et_2). MS: *m/z* (%): 498 (M^+, 2), 361(M^+ – PO_3Et_2, 100), 393(M^+ – COPh, 100), 105 (COPh, 50). Elemental analysis for $C_{30}H_{27}O_5P$ (498.5) calcd.: C, 72.28; H, 5.46; found: C, 72.3; H, 5.4%.

Diethyl [2-oxo-2-phenyl-1-(2-phenylnaphtho[2,1-*b*]furan-1-yl)ethyl]phosphonate (7). Yield 40%. Yellow powder. M.p. 139–142°C. IR (KBr) (ν_{max}/cm^{-1}): 1617 (C=O), 1481 (P–O). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.99, and 1.10 (6 H, 2 t, $^3J_{HP}$ = 7.0 Hz, 2 Me), 3.93, and 4.11 (4H, m, 2OCH$_2$), 5.71 (1 H, d, $^2J_{HP}$ = 3.6 Hz, CH), 7.04–7.57 (10 H, m, 10 CH), 7.62 (1 H, d, $^3J_{HH}$ = 8.0 Hz, CH), 7.75 (2 H, d, $^3J_{HH}$ = 8.9 Hz, 2 CH$_{ortho}$ of Ph), 7.81 (1 H, d, $^3J_{HH}$ = 7.4 Hz, CH), 7.99 (2 H, d, $^3J_{HH}$ = 7.8 Hz, 2 CH$_{ortho}$ of COPh); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 16.34, and 16.38 (2d, $^3J_{CP}$ = 5.6 Hz, 2Me), 64.36 and 64.01 (2d, $^2J_{CP}$ = 7.3 Hz, 2OCH$_2$), 79.50 (d, $^1J_{CP}$ = 173.6, C–P), 117.92 (C), 124.51, 124.83, 125.08, and 126.01 (4 CH), 127.32 (d, $^3J_{CP}$ = 3.8 Hz, 2 CH$_{ortho}$ of Ph), 128.59, and 128.70 (3 CH), 129.50 (C), 129.62 (2 CH), 129.91 (C), 131.80, and 132.63 (2 CH), 133.71 (C), 136.62 (C), 151.40 (d, $^3J_{CP}$ = 13.7 Hz, C–O), 195.12 (C=O); ^{31}P NMR (202.4 MHz, $CDCl_3$): δ = 16.37 (PO_3Et_2). MS: *m/z* (%): 498 (M^+, 2), 361(M^+ – PO_3Ee_2, 100), 393 (M^+ – COPh, 100), 105 (COPh, 50). Elemental analysis for $C_{30}H_{27}O_5P$ (498.5) calcd.: C, 72.28; H, 5.46; found: C, 72.3; H, 5.4%.

REFERENCES

1. Lindell S.D., in *Comprehensive Organic Functional Group Transformations*, Elsevier Science Ltd. Pergamon, 1st edn. p. 1007 (1995).
2. 1. (a) Olah G.A. and Calin A., *J. Am. Chem Soc.*, **90**, 938 (1968); (b) Childs R.F., Faggiani R., Lock C.J.L., Mahendran M. and Zweep S.D., *J. Am. Chem. Soc.*, **108**, 1692 (1986).
3. (a) Mir-Mohamad-Sadeghy M. and Rickborn B., *J. Org. Chem.*, **48**, 2237 (1983); (b) Cornejo J.J., Ghodsi S., Johnson R.D., Woodling R. and Rickborn B., *J. Org. Chem.*, **48**, 3869 (1983); (c) Ohmura H. and Mikami K., *Tetrahedron Lett.*, **42**, 6859 (2001).

4. Olah G.A. and Svoboda J.J., *Synthesis*, 306 (1972).
5. (a) Joule J.A., Mills K. and Smith G.F., *Heterocyclic Chemistry*, Chapman & Hall, London 3rd edn, pp. 146–183 (1995); (b) Fichtner C., Remennikov G. and Mayr H., *Eur. J. Org. Chem*., 4451 (2001); (c) Lu Y. and Foo L., *Tetrahedron Lett.*, **43**, 715 (2002).
6. Basavaiah D., Sreenivasulu B. and Rao J.S., *Tetrahedron Lett.*, **42**, 1147 (2001).
7. Yavari I., Anary-Abbasinejad M. and Alizadeh A., *Tetrahedron Lett*., **43**, 4503 (2002).
8. Tebby J.C., Verkede J.G. and Quin L.D., *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, VCH Publishers: Weinheim; ch. 1, p. 34 (1987).
9. Skattebol L., Jones E.R.H. and Whiting M.C., *Org. Synth. Coll. Vol.*, **4**, 792 (1963).
10. Bowden K., Heilbron I.M., Jones E.R.H. and Weedon B.C., *J. Chem. Soc.*, 39 (1946).