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Study of the Pyrolytic Chemistry of Isobenzofurylmethyl Benzoates

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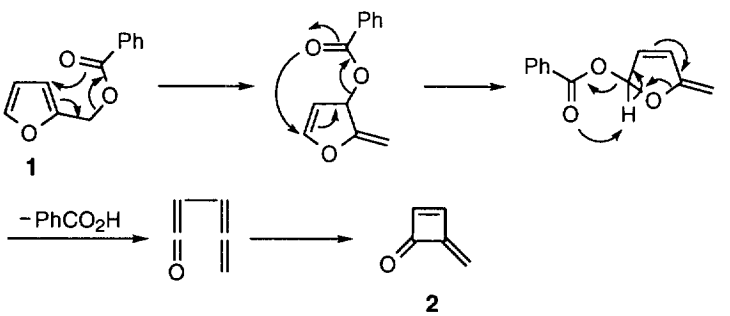
Abstract: Pyrolysis of (1-isobenzofuryl)methyl benzoate (**9a**), produced in situ from flash vacuum pyrolysis of (7-oxa-1-benzonorbornenyl)methyl benzoate (**10a**), gave methylenebenzocyclobutenone (**4**), 2-ethynylbenzaldehyde (**5**) and benzocyclopentadienone (**6**). The deuterium-labeled study indicated that the mechanism for the formation of these products involved the double migrations of benzoate group in **9a**. Pyrolysis of (3-methyl-1-isobenzofuryl)methyl benzoate (**9c**) gave 1,3-dimethylene-1,3-dihydroisobenzofuran (**33**), which is stable in benzene and hydrolyzed rapidly in chloroform to give 1,2-diacetylbenzene (**35**). © 1997 Elsevier Science Ltd.

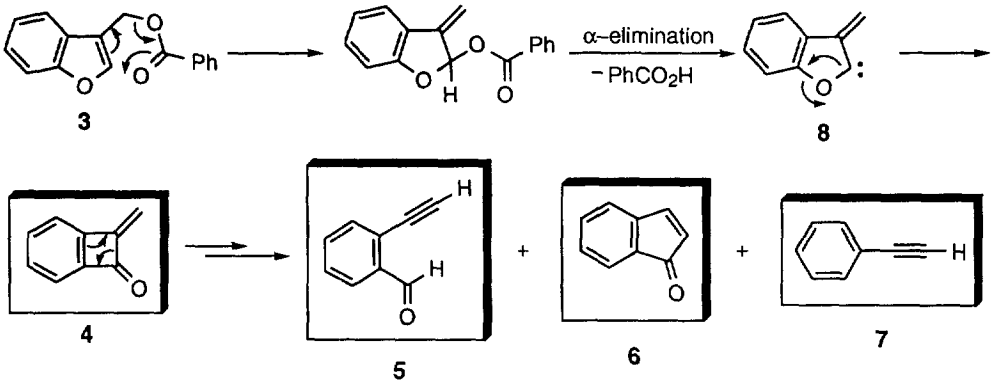
INTRODUCTION

Trahanovsky and Park have reported that flash vacuum pyrolysis (FVP) of (2-furyl)methyl benzoate (**1**) gives methylenecyclobutenone (**2**).[1] The mechanism for the formation of **2** involves double migrations of benzoate group in **1** into the furan ring (Scheme 1).[2]



Scheme 1

Like the pyrolytic chemistry of **1**, the benzoate group migration pathway was also observed in the FVP of (3-benzofuryl)methyl benzoate (**3**) to give several novel products, such as methylenebenzocyclobutenone (**4**), 2-ethynylbenzaldehyde (**5**), benzocyclopentadienone (**6**) and ethynylbenzene (**7**), via a carbene intermediate **8** (Scheme 2).[3]

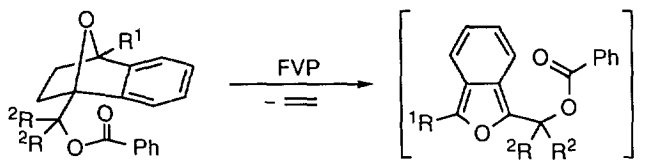


Scheme 2

Due to high reactivity of the isobenzofuran system,[4-6] there has been no report on the chemistry of (1-isobenzofuryl)methyl benzoate (**9a**). Nevertheless, the novelty of the gas phase reactions of **1** and **3**[2,3,7] has attracted our interests and prompted us to study the pyrolytic chemistry of **9a**, its deuterated derivative, (1-isobenzofuryl)-α,α-dideuteriomethyl benzoate (**9b**), and its methylated derivative, (3-methyl-1-isobenzofuryl)methyl benzoate (**9c**). The results of this study are presented herein.

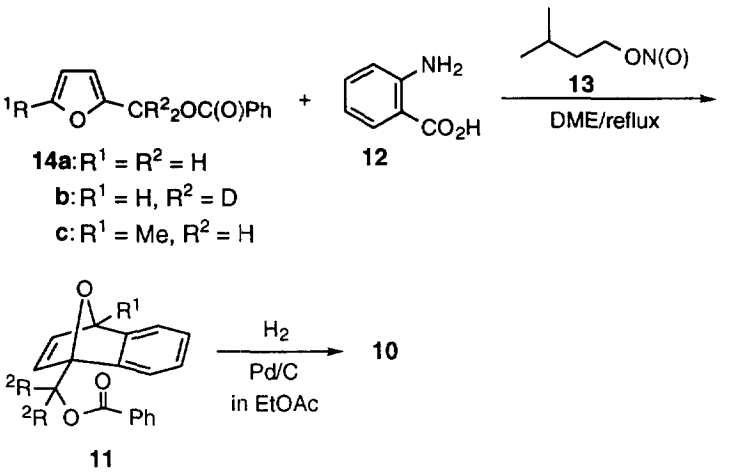
RESULTS AND DISCUSSION

We chose (7-oxa-1-benzonorbornenyl)methyl benzoate (**10a**), (7-oxa-1-benzonorbornenyl)-α,α-dideuteriomethyl benzoate (**10b**) and (4-methyl-7-oxa-1-benzonorbornenyl)methyl benzoate (**10c**) as the pyrolysis precursors from which **9a-c** could be formed in situ via retro Diels-Alder reactions[4] of **10a-c** (Eq. 1), respectively.



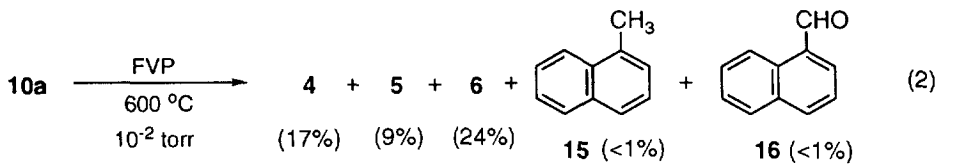
10a: $R^1 = R^2 = H$ **9a**: $R^1 = R^2 = H$
b: $R^1 = H, R^2 = D$ **b**: $R^1 = H, R^2 = D$
c: $R^1 = Me, R^2 = H$ **c**: $R^1 = Me, R^2 = H$

Syntheses of (7-Oxa-1-benzonorbornenyl)methyl Benzoates 10a-c. The general procedure for synthesis of **10a-c** is outlined in Scheme 3. **10a-c** are prepared from hydrogenation of the strained double bonds of (7-oxa-1-benzonorbornadienyl)methyl benzoates **11a-c**. **11a-c** can be generated by Diels-Alder reactions of benzyne, produced in situ by reaction of anthranilic acid (**12**) with isoamyl nitrite (**13**) in refluxing 1,2-dimethoxyethane (DME),[8] with the corresponding benzoates **14a-c**.[4,9]



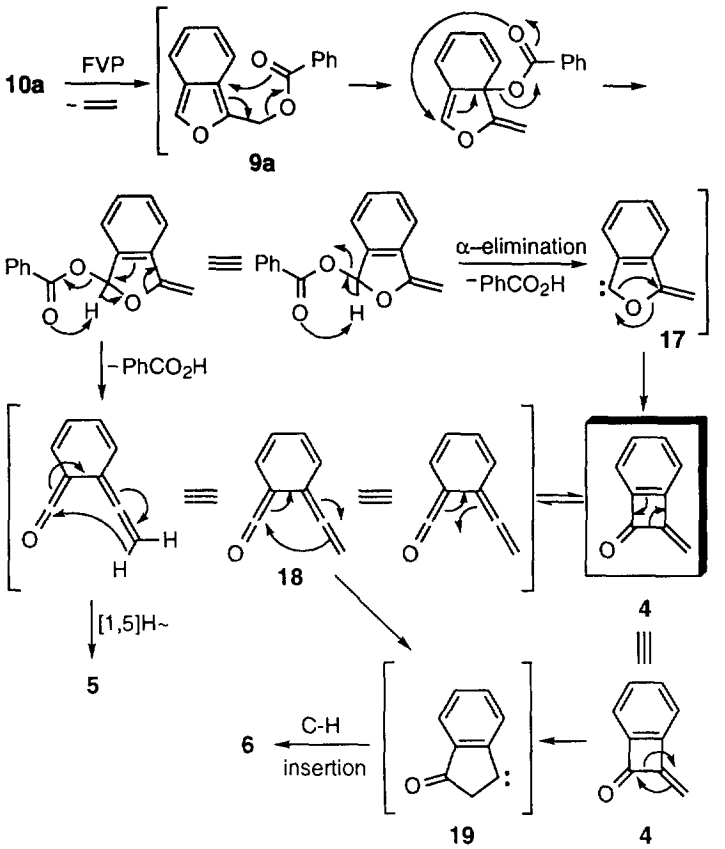
Scheme 3

Preparation and Pyrolysis of (1-Isobenzofuryl)methyl Benzoate (9a). The FVP of **10a** was performed at 600 °C and ca. 0.01 torr by using the method previously reported.[10] Methylenebenzocyclobutenone (**4**), 2-ethynylbenzaldehyde (**5**) and benzocyclopentadienone (**6**) were produced as major products along with two minor products, they are 1-methylnaphthalene (**15**) and 1-naphthaldehyde (**16**) (Eq. 2). When the pyrolysis



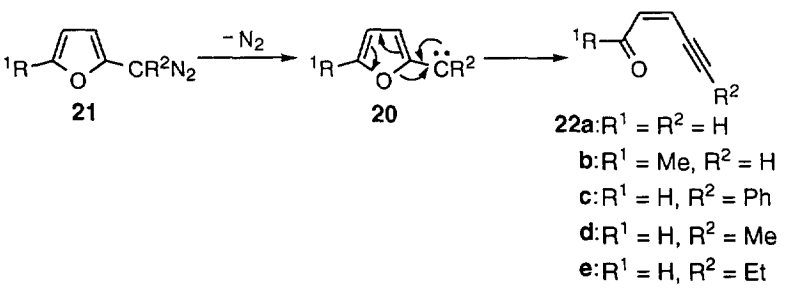
temperature was raised to 700 °C, **6** was obtained as the sole product. A proposed mechanism to account for the formation of the pyrolysis products **4**, **5** and **6** is presented in Scheme 4.[11]

Similar to the pyrolytic chemistry of **1**,[2] the benzoate group in (1-isobenzofuryl)methyl benzoate (**9a**), generated via retro Diels-Alder reaction of **10a**, underwent double migrations and inserted into the isobenzofuran ring. A subsequent α-elimination gave the carbene intermediate **17** or allene-ketene **18**. Compound **4** could be produced either from carbene **17** via a ring-contraction process or from **18** via an intramolecular [2+2] reaction. Ring-expansion of **4** or ring-closure of **18** could give carbene intermediate **19**, which can undergo a C-H insertion reaction to give benzocyclopentadienone (**6**). Finally, a 1,5-H shift of **18** gave 2-ethynylbenzaldehyde (**5**).

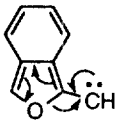


Scheme 4

Hoffman and Shechter reported that furfurylidene **20**, produced by thermolysis of the corresponding diazo compound **21**, gave ring-opening products γ,δ-acetylenic-α,β-olefinic carbonyl compound **22** (Scheme 5).[12] By the same token, we anticipated that carbene intermediate **23**, if generated from α-elimination of **9a**, would also undergo a ring-opening process to give 2-ethynylbenzaldehyde (**5**) (Eq. 3).



Scheme 5

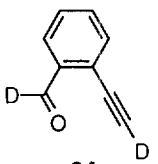


23

5 (3)

In order to confirm that if carbene intermediate **23** is involved in the pyrolysis reaction of **9a**, (7-oxa-1-benzonorbornenyl)-α,α-dideuteriomethyl benzoate (**10b**) was prepared and pyrolyzed.

The pyrolysate from FVP of **10b** was collected in $CDCl_3$ and examined by ^1H NMR spectroscopy. In comparison, the peaks at δ 10.54 (-C(O)-H) and 3.48 (-C≡H) in the ^1H NMR spectrum of pyrolysate of **10a** were not visible in that of the pyrolysate of **10b**. The disappearance of these two peaks indicates that dideuterium-labeled aldehyde **24** is formed instead of monodeuterium-labeled aldehyde **25**. Thus, based on the above results, we exclude the possibility of participation of the carbene intermediate **23** in this pyrolytic reaction.



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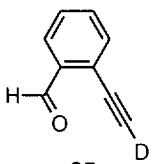
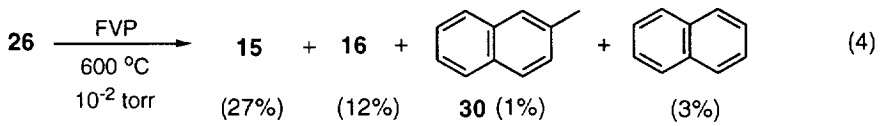


25

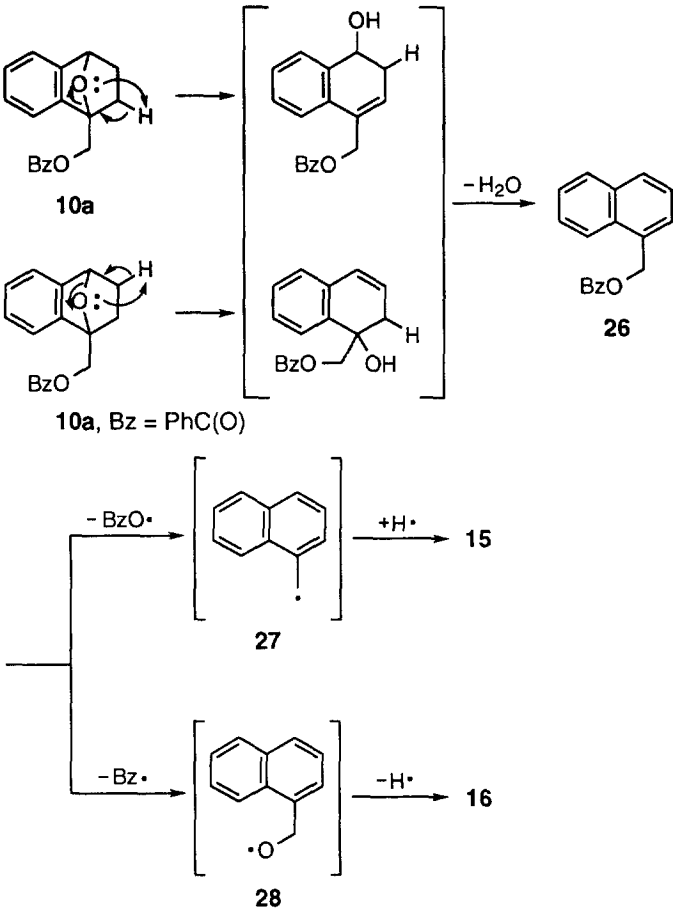
As for the formation of minor products **15** and **16**, one possible pathway might involve the formation of (1-naphthalenyl)methyl benzoate (**26**) which is generated by eliminating a molecule of H_2O from **10a**. **26** could experience a homolytic cleavage of the C-O or O-C(O) bond under pyrolysis conditions to give radical **27** or **28** respectively. Radical **27** or **28** could further abstract or lose a hydrogen radical to form 1-methylnaphthalene (**15**) or 1-naphthaldehyde (**16**), respectively (Scheme 6).

In order to prove that **26** was the pyrolysis precursor of **15** and **16**, we synthesized and pyrolyzed **26**. GC/MS analysis of the pyrolysate of **26** showed that 1-methylnaphthalene (**15**) and 1-naphthaldehyde (**16**) were formed as the major products with two minor products, they are 2-methylnaphthalene (**30**) and naphthalene (Eq. 4).



(4)

This result accords with the mechanism we proposed to account for the formation of **15** and **16** described in Scheme 6.

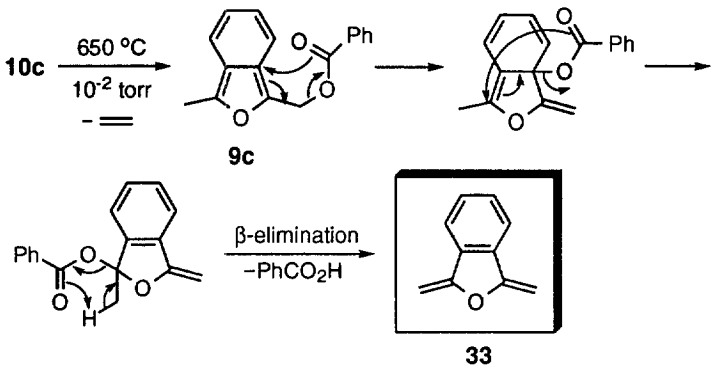


Scheme 6

Preparation and Pyrolysis of (3-Methyl-1-isobenzofuryl)methyl Benzoate (9c). We have synthesized and studied the chemistry of 2,5-dimethylene-2,5-dihydrofuran (**31**), the furan analogue of *p*-quinodimethane (**32**),[13] by FVP of (5-methyl-2-furyl)methylbenzoate (**14c**)[14] a few years ago.

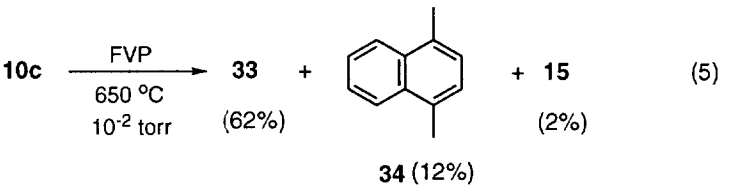
31 **32**

Based on the formation mechanisms of methylenecyclobutenone (**2**)[2] (Scheme 1) and **31**,[3] produced by FVP of benzoates **1** and **14c** respectively, and the pyrolysis results of **9a** and **9b** described above, we anticipate that 1,3-dimethylene-1,3-dihydroisobenzofuran (**33**), the isobenzofuran analogue of *p*-quinodimethane (**32**), could be formed from the FVP of **9c** (Scheme 7).



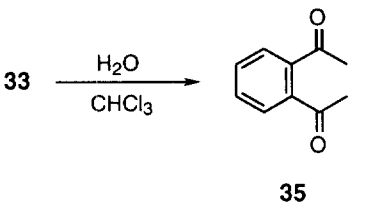
Scheme 7

10c, prepared by the general synthetic route described in Scheme 3, was then pyrolyzed at 650 °C and ca. 0.01 torr and found to give 1,3-dimethylene-1,3-dihydroisobenzofuran (**33**) as the major product along with two minor ones, 1,4-dimethylnaphthalene (**34**) and 1-methylnaphthalene (**15**) (Eq. 5). Compound **33** is stable in



(5)

benzene at room temperature for several hours and at 0 °C for more than three weeks. When treated with chloroform, **33** was hydrolyzed rapidly to give 1,2-diacetylbenzene (**35**) as the sole product (Eq. 6).



(6)

We had reported that 2,5-dimethylene-2,5-dihydrofuran (**31**) reacts with various trapping agents to form one-on-one, two-on-one and two-on-two adducts.[14] However, possibly due to the instability of the isobenzofuran moiety, attemps to trap **33** with trapping agents such as bromine, thiophenol, methanol, ethanol, diethylamine and acetic acid all resulted in failure.

EXPERIMENTAL SECTION

Melting points were determined with a MEL-TEMP apparatus and are uncorrected. Infrared spetra were recorded with a Shimadzu IR-408 and Bio-Rad Win-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured with a Varian VXR-300 NMR spectrometer, with tetramethylsilane as the internal standard. GC/MS analyses were performed on a Hewlett-Packard (HP) 5890 II GC equipped with a 30 m x 0.25 mm (i.d.) capillary column (DB-5) and with a HP-5971 mass spectral detector. Mass spectra were recorded with a VG QUATTRO 5022 spectrometer. The pyrolysis products 1-methylnaphthalene (**15**), 1-naphthaldehyde (**16**), 2-methylnaphthalene (**30**), naphthalene, 1,2-diacetylbenzene (**34**) and 1,4-dimethylnaphthalene (**35**) were identified by comparison of their GC and MS spectral data with those of authentic samples.

(2-Furyl)methyl Benzoate (14a). (2-Furyl)methyl alcohol (10.00 g, 102.04 mmol) was converted to benzoate **14a** by using the procedure reported previously for the synthesis of (2-methyl-3-furyl)methyl benzoate.[15] The benzoate was purified by column chromatography on silica gel (5% ethyl acetate in hexanes) to yield **14a** (19.00 g, 94.06 mmol, 92% yield): IR (neat, cm^{-1}) 1725, 1270, 1100, 1070; [lit.[1] IR (CCl_4) 1720, 1265, 1250, 1105, 1090]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07-8.04 (m, 2H), 7.55-7.53 (m, 1H), 7.45-7.40 (m, 3H), 6.49 (d, J=3.0 Hz, 1H), 6.38 (dd, J=3.0 and 1.6 Hz, 1H), 5.31 (s, 2H); [lit.[1] ^{1}H NMR (neat) δ 8.82-7.83 (m, 2H), 7.38 (m, 1H), 7.33-7.00 (m, 3H), 6.44 (d, J=3.2 Hz, 1H), 6.26 (dd, J=3.2 and 1.8 Hz, 1H), 5.30 (s, 2H)]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.22, 149.53, 143.27, 133.06, 129.88, 129.73, 128.32, 110.76, 110.56, 58.49; MS (LR, 70 eV) m/z (%) 202 (M^+, 30), 105 (100), 81 (95), 77 (32), 53 (18), 52 (12), 51 (18); Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.30; H, 5.01.

(7-Oxa-1-benzonorbornadienyl)methyl Benzoate (11a). To a boiling solution of the mixture of benzoate **14a** (1.20 g, 5.94 mmol) and isoamyl nitrite (**13**) (0.80 g, 6.84 mmol) in 1,2-dimethoxyethane (DME, 30 mL) was added dropwise into the solution of anthranilic acid (**12**) (0.94 g, 6.86 mmol) in DME (20 mL). After completion of addition, the reaction mixture was refluxed for another 2 h. The solvent was removed and the crude product was separated by column chromatography on silica gel (10% ethyl acetate in hexanes, Rf=0.3) to yield **11a** (0.97 g, 3.49 mmol, 58% yield): mp 84-85 °C; IR (in $CHCl_3$, cm^{-1}) 3060, 3010, 2890, 1720, 1600, 1580; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08-8.05 (m, 2H), 7.56-7.51 (m, 1H), 7.42-7.37 (m, 2H), 7.26-7.22 (m, 2H), 7.08-7.06 (m, 1H), 6.99-6.92 (m, 3H), 5.74 (d, J=1.8 Hz, 1H), 5.25 (d, J=12.6 Hz, 1H), 5.06 (d, J=12.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.29, 150.01, 147.87, 144.74, 142.04, 133.12, 129.74, 129.51, 128.30, 125.16, 125.00, 120.20, 119.38, 91.02, 82.25, 61.78; MS (LR, 30 eV) m/z (%) 278 (M^+, 1), 252 (4), 163 (30), 156 (16), 131 (33), 129 (16), 128 (75), 115 (18), 106 (27), 105 (100), 77 (25); HRMS Calcd for $C_{18}H_{14}O_3$: 278.0943. Found: 278.0938; Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.51; H, 5.10.

(7-Oxa-1-benzonorbornenyl)methyl Benzoate (10a). To a 100 mL round-bottomed flask containing a solution of **11a** (0.50 g, 1.80 mmol) in ethyl acetate (50 mL) was added a catalytic amount of 5% Pd/C. The reaction system was evacuated to approximately 20-30 torr to exclude air and then connected with a balloon filled with H_2 gas. The reaction mixture was stirred at room temperature until the H_2 gas was exhausted. After filtration, and removal of the solvent from filtrate, **10a** was obtained in quantitative yield. Compound **10a**: mp 56-57 °C; IR (in $CHCl_3$, cm^{-1}) 3010, 2950, 2860, 1720, 1600, 1585; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06-8.03

(m, 2H), 7.57-7.52 (m, 1H), 7.43-7.38 (m, 2H), 7.28-7.18 (m, 4H), 5.44 (d, J=5.1 Hz, 1H), 5.07 (dd, J=18.3 and 12.6 Hz, 2H), 2.25-2.21 (m, 1H), 2.07-2.01 (m, 1H), 1.50-1.48 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.40, 146.10, 144.42, 133.07, 129.77, 128.33, 126.81, 126.60, 118.90, 118.10, 86.81, 78.94, 63.27, 28.58, 28.46; MS (LR, 30 eV) m/z (%) 280 (M^+, 1), 253 (12), 252 (66), 132 (12), 131 (100), 105 (78), 103 (16), 102 (13), 77 (17); Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.13; H, 5.75. Found: C, 76.72; H, 5.74.

General Pyrolysis Procedure.[10] The furnace was maintained at temperatures in the range 600-700 °C. A sample for pyrolysis was placed into the sample chamber and the system was evacuated to ca. 0.01 torr. The sample chamber was heated to ca. 100 °C during the pyrolysis. A condenser cooled to ca. 0 °C was inserted between the furnace and the liquid-nitrogen-cooled trap to collect the benzoic acid formed as a by-product. During the pyrolysis $CHCl_3$ (or $CDCl_3$, C_6D_6 in some case) was deposited into the trap through a side arm. After pyrolysis was completed, the trap was warmed to room temperature, a certain amount of solvent was added to rinse the walls of the trap. The product solution was then collected for product analysis.

Pyrolysis of (7-Oxa-1-benzonorbornenyl)methyl Benzoate (10a). A 0.40 g (1.43 mmol) quantity of **10a** was pyrolyzed at 600 °C and ca. 0.01 torr by using the general pyrolysis procedure. Methylenebenzocyclobutenone (**4**) (30.6 mg, 0.24 mmol, 17% yield), 2-ethynylbenzaldehyde (**5**) (16.6 mg, 0.13 mmol, 9% yield) and benzocyclopentadienone (**6**) (44.0 mg, 0.34 mmol, 24% yield) were formed as major products with 1-methylnaphthalene (**15**) (<1%) and 1-naphthaldehyde (**16**) (<1%) as minor ones. Products **4** and **5** were identified by comparison of the ^{1}H and/or ^{13}C NMR spectra to those reported in the literatures.[3,16] The yields of these pyrolysis products were measured by quantitative analysis of GC with weighed diphenylmethane as an internal standard. Compound **4**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.6-7.3 (m, 4H), 5.48 (d, J=1.5 Hz, 1H), 5.25 (d, J=1.5 Hz, 1H); [lit.[3] ^{1}H NMR ($CDCl_3$) δ 7.5-7.3 (m, 4H), 5.47 (d, J=1.47 Hz, 1H), 5.24 (d, J=1.46 Hz, 1H)]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.00, 159.47, 156.20, 155.90, 135.02, 130.16, 121.51, 120.11, 102.02; [lit.[3] ^{13}C NMR ($CDCl_3$) δ 186.1, 159.6, 156.4, 156.1, 135.0, 130.2, 121.6, 120.2, 102.1]; GC/MS (LR, 70 eV) m/z (%) 130 (M^+, 59), 102 (100), 76 (31), 75 (14), 74 (17), 50 (11); [lit.[3] GC/MS (LR, 20 eV) m/z (%) 130 (100), 103 (3.2), 102 (38.6), 76 (1.2), 75 (0.6)]. Compound **5**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.54 (s, 1H), 7.70-7.30 (m, 4H), 3.48 (s, 1H); [lit.[16] ^{1}H NMR ($CDCl_3$) δ 10.43 (s, 1H), 8.00-7.30 (m, 4H), 3.46 (s, 1H)]; GC/MS (LR, 70 eV) m/z (%) 130 (M^+, 82), 103 (10), 102 (100), 101 (22), 76 (31), 75 (22), 74 (20). Compound **6**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, J=6.0 Hz, 1H), 7.43 (d, J=7.2 Hz, 1H), 7.34-7.20 (m, 2H), 7.06 (d, J=7.2 Hz, 1H), 5.89 (d, J=6.0 Hz, 1H); [lit.[17] ^{1}H NMR ($CDCl_3$) δ 7.51 (d, J=6.0 Hz, 1H), 7.39 (dd, J=7.0 and 1.5 Hz, 1H), 7.23 (m, 2H), 7.00 (d, J=7.0 and 1.5 Hz, 1H), 5.83 (d, J=6.0 Hz, 1H)]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.42, 149.78, 144.62, 133.65, 130.38, 129.14, 127.19, 122.66, 122.23; GC/MS (LR, 70 eV) m/z (%) 130 (M^+, 74), 102 (100), 76 (21), 75 (14), 74 (15), 50 (10).

Benzocyclopentadienone (6). The pyrolysate from FVP of **10a** (65 mg, 0.21 mmol) at 700 °C and ca. 0.01 torr was collected in $CHCl_3$. After removal of $CHCl_3$, the residue was separated by column chromatography on silica gel (10% ethyl acetate in hexanes) to give **6** (20 mg, 0.15 mmol, 66% yield).

(2-Furyl)-α,α-dideuteriomethyl Benzoate (14b). To a slurry of $LiAlD_4$ (1.42 g, 33.81 mmol) in dry THF (30 mL) at 0 °C was slowly added a solution of 2-furoyl chloride (2.00 g, 15.38 mmol) in dry THF (30 mL). The

mixture was stirred at 0 °C for 2 h and a standard workup[18] gave (2-furyl)-α,α-dideuteriomethyl alcohol (**39**) (1.38 g, 13.80 mmol, 90% yield): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.35 (d, J=1.8 Hz, 1H), 6.30 (dd, J=2.6 and 1.8 Hz, 1H), 6.23 (d, J=2.6 Hz, 1H), 3.81 (br, 1H). Without further purification, alcohol **39** (1.00 g, 10.00 mmol) was converted to **14b**, using the procedure described for synthesis of **14a**. The benzoate was purified by column chromatography on silica gel (5% ethyl acetae in hexanes) to yield **14b** (1.80 g, 8.82 mmol, 88%): IR (neat, cm^{-1}) 3120, 3060, 2080, 1720, 1600, 1585; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06-8.03 (m, 2H), 7.56-7.51 (m, 1H), 7.44-7.38 (m, 3H), 6.48 (dd, J=3.3 and 0.9 Hz, 1H), 6.37 (dd, J=3.3 and 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.18, 149.46, 143.23, 133.01, 129.86, 129.70, 128.29, 110.53, 58.53, 58.23, 57.93, 57.62, 57.33; MS (LR, 70 eV) m/z (%) 204 (M^+, 47), 105 (78), 84 (15), 83 (100), 81 (12), 77 (64), 55 (42), 53 (19), 51 (30), %0 (11); Anal. Calcd for $C_{12}H_8D_2O_3$: C, 70.58; H, 4.94. Found: C, 70.55; H, 5.04.

(7-Oxa-1-benzonorbornadienyl)-α,α-dideuteriomethyl Benzoate (11b). **11b** (1.52 g, 5.43 mmol, 74% yield) was prepared by reacting benzoate **14b** (1.50 g, 7.35 mmol) with anthranilic acid (**12**) (1.30 g, 9.49 mmol) and isoamyl nitrite (**13**) (1.12g, 9.57 mmol) in a similar way to the formation of **11a**. Compound **11b**: mp 80-82 °C; IR (neat, cm^{-1}) 3075, 3010, 1720, 1620, 1585; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08-8.05 (m, 2H), 7.53-7.51 (m, 1H), 7.43-7.38 (m, 2H), 7.25-7.23 (m, 2H), 7.09-7.06 (m, 1H), 7.00-6.92 (m, 3H), 5.74 (d, J=2.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.30, 149.98, 147.84, 144.73, 142.03, 133.12, 129.73, 129.50, 128.30, 125.16, 125.00, 120.20, 119.38, 90.92, 82.25, 61.78, 61.50, 61.20, 60.91, 60.62; MS (LR, 70 eV) m/z (%) 280 (M^+, 0.5), 264 (1.5), 254 (1.3), 158 (17), 130 (50), 105 (100), 77 (27).

(7-Oxa-1-benzonorbornenyl)-α,α-dideuteriomethyl Benzoate (10b). **11b** was hydrogenated over 5% Pd/C in a similar way to the formation of **10a** to yield **10b** quantitatively. Compound **10b**: mp 61-62 °C; IR (neat, cm^{-1}) 1725; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06-8.03 (m, 2H), 7.57-7.52 (m, 1H), 7.44-7.39 (m, 2H), 7.28-7.18 (m, 4H), 5.44 (d, J=5.1 Hz, 1H), 2.24-2.10 (m, 1H), 2.07-2.01 (m, 1H), 1.51-1.47 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.44, 146.10, 144.41, 133.08, 129.78, 128.34, 126.83, 126.61, 118.92, 118.12, 86.72, 78.97, 63.30, 63.00, 62.70, 62.40, 62.10, 28.54, 28.46; MS (LR, 30 eV) m/z (%) 282 (M^+, 2), 255 (48), 254 (95), 149 (15), 134 (38), 133 (100), 132 (17), 131 (51), 117 (17), 115 (15), 106 (24), 105 (93), 103 (27), 77 (20); HRMS Calcd for $C_{18}H_{14}D_2O_3$: 282.1225. Found: 282.1224. Anal. Calcd for $C_{18}H_{14}D_2O_3$: C, 82.42; H, 5.38. Found: C, 82.33; H, 5.43.

(1-Naphthalenyl)methyl Benzoate (26). 1-Naphthalenemethanol (**29**) (1.92 g, 12.15 mmol) was converted to benzoate **26** by using the procedure described for synthesis of **14a**. The benzoate was purified by column chromatography on silica gel (5% ethyl acetate in hexanes) to yield **26** (2.82 g, 10.76 mmol, 89% yield): mp 36-37 °C; IR (neat, cm^{-1}) 3100, 2900, 1725, 1600, 1580, 1520; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07-8.03 (m, 3H), 7.88-7.85 (m, 2H), 7.62-7.36 (m, 7H), 5.81 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.42, 133.71, 132.97, 131.71, 131.47, 130.05, 129.69, 129.29, 128.69, 128.31, 127.44, 126.58, 125.92, 125.25, 123.57, 65.08; GC/MS (LR, 70 eV) m/z (%) 262 (M^+, 43), 141 (77), 140 (31), 139 (20), 115 (25), 105 (100), 77 (22); Anal. Calcd for $C_{16}H_{14}O_2$: C, 76.57; H, 5.71. Found: C, 76.43; H, 5.69.

Pyrolysis of (1-Naphthalenyl)methyl Benzoate (26). A 0.05 g (0.19 mmol) quantity of benzoate **26** was pyrolyzed at 600 °C and ca. 0.01 torr by using the general pyrolysis procedure. Quantitative GC analysis with

weighed diphenylmethane as an internal standard indicated that pyrolysis of benzoate **26** gave 27% yield of **15**, 12% yield of **16**, 1% yield of **30** and 3% yield of naphthalene.

(5-Methyl-2-furyl)methyl Benzoate (14c). (5-Methyl-2-furyl)methanol (5.50 g, 49.11 mol), obtained by reducing 5-methylfurfural (**40**) with lithium aluminum hydride,[14] was converted to benzoate **14c**, using the procedure described for synthesis of benzoate **14a**. The benzoate was purified by column chromatography on silica gel (5% ethyl acetae in hexanes) to give **14c** (9.76 g, 45.18 mmol, 92% yield): IR (neat, cm^{-1}) 3060, 2960, 2930, 1720, 1565, 1460, 1275; [lit.[3] IR ($CHCl_3$, cm^{-1}) 1715, 1265, 1100, 1089]; ^1H NMR (300 MHz, $CDCl_3$) δ 8.10-7.35 (m, 5H), 6.36 (d, J=2.7 Hz, 1H), 5.96 (m, 1H), 5.25 (s, 2H), 2.30 (s, 3H); [lit.[3] ^1H NMR ($CDCl_3$) δ 8.00-7.12 (m, 5H), 6.35 (d, J=3.2 Hz, 1H), 5.91 (m, 1H), 5.22 (s, 2H), 2.28 (s, 3H)]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.25, 153.13, 147.68, 132.93, 130.05, 129.70, 128.25, 111.82, 106.56, 58.72, 13.58; MS (LR, 70 eV) m/z (%) 216 (M^+), 105, 95 (100), 94, 79, 77, 51; Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.28; H, 5.57.

(4-Methyl-7-oxa-1-benzonorbornadienyl)methyl Benzoate (11c). **11c** (0.50 g, 1.71 mmol, 69% yield) was prepared by reacting benzoate **14c** (0.54 g, 2.50 mmol) with anthranilic acid (**12**) (0.38 g, 2.77 mol) and isoamyl nitrite (**13**) (0.33, 2.82 mmol) in the similar way to the formation of **11a**. Compound **11c**: mp 91-92 °C; IR (in $CHCl_3$, cm^{-1}) 3020, 1720, 1600, 1458, 1390; ^1H NMR (300 MHz, $CDCl_3$) δ 8.09-8.06 (m, 2H), 7.56-7.53 (m, 1H), 7.45-7.40 (m, 2H), 7.23-7.16 (m, 2H), 7.02-6.94 (m, 3H), 6.85-6.83 (m, 1H), 5.21 (d, J=12.6 Hz, 1H), 5.02 (d, J=12.6 Hz, 1H), 1.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.42, 152.38, 149.44, 147.21, 143.34, 133.16, 129.84, 129.63, 128.35, 125.19, 124.84, 119.05, 118.70, 90.23, 89.40, 62.10, 15.13; MS (LR, 70 eV) m/z (%) 292 (M^+, 0.5), 266 (2), 252 (6), 163 (11), 145 (35), 129 (16), 128 (100), 105 (95), 77 (13); Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.74; H, 5.54.

(4-Methyl-7-oxa-1-benzonorbornenyl)methyl Benzoate (10c). **11c** was hydrogenated over 5% Pd/C in the similar way to the formation of **10a** to yield **10c** quantitatively. Compound **10c**: mp 56-58 °C; IR (in $CHCl_3$, cm^{-1}) 3070, 3020, 2980, 2940, 2870, 1720, 1600; ^1H NMR (300 MHz, $CDCl_3$) δ 8.8.06-8.04 (m, 2H), 7.56-7.51 (m, 1H), 7.42-7.37 (m, 2H), 7.26-7.16 (m, 4H), 5.03 (dd, J=14.1 and 12.6 Hz, 2H), 2.22-2.16 (m, 1H), 1.99-1.93 (m, 1H), 1.87 (s, 3H), 1.60-1.51 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.39, 148.22, 145.19, 133.00, 129.75, 128.27, 126.80, 126.46, 117.93, 117.58, 85.86, 85.54, 63.54, 34.52, 31.27, 17.52; MS (LR, 30 eV) m/z (%) 294 (M^+, 0.4), 276 (0.8), 267 (16), 266 (69), 161 (25), 146 (26), 145 (100), 144 (11), 129 (21), 105 (49), 77 (10); Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.56; H, 6.35.

Pyrolysis of (4-Methyl-7-oxa-1-benzonorbornenyl)methyl Benzoate (10c). **10c** (1.20 g, 4.08 mmol) was pyrolyzed at 650 °C and ca. 0.01 torr by using the general pyrolysis procedure. The pyrolysate was kept in benzene-d_6, and the ^1H and ^{13}C NMR spectra showed that 1,3-dimethylene-1,3-dihydroisobenzofuran (**33**) was the main pyrolysis product of **10c**. Quantitative ^1H NMR analysis, using weighed 1,2-dibromoethane as the internal standard, indicated that 62% of **33** was obtained from FVP of **10c**. Compound **33**: IR (in C_6D_6, cm^{-1}) 1656, 1474; ^1H NMR (300 MHz, C_6D_6) δ 7.16-7.08 (m, 2H), 6.94-6.91 (m, 2H), 4.78 (d, J=2.4 Hz, 2H), 4.55 (d, J=2.4 Hz, 2H); ^{13}C NMR (75 MHz, C_6D_6) δ 158.69, 134.56, 129.78, 120.98, 82.36; MS (LR, 70 eV) m/z (%) 144 (M^+, 23), 116 (29), 115 (100); Quantitative GC analysis with weighed diphenylmethane showed that, besides **33**, pyrolysis of **10c** also gave 12% yield of **34** and 2% yield of **15**.

1,2-Diacetylbenzene (35). **10c** (0.20 g, 0.68 mmol) was pyrolyzed at 650 °C and ca. 0.01 torr in the normal manner. The pyrolysate, collected in $CHCl_3$, was dried over $MgSO_4$ and after removal of the solvent, the residue was purified by column chromatography on silica gel (25% ethyl acetate in hexane) to give **35** (0.04 g, 0.25 mmol, 36% yield): ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 (s, 4H), 2.54 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.76, 139.42, 131.05, 127.71, 28.71; MS (LR, 30 eV) m/z (%) 162 (M^+, 0.7), 147 (100), 91 (32).

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