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Pyrolytic Chemistry of (1-Isonaphthofuryl)methyl Benzoate

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Abstract: Flash vacuum pyrolysis of (1-isonaphthofuryl)methyl benzoate (**6**) at temperatures in the range 550-700 °C and ca. 10^{-2} torr gave methylenenaphthocyclobutenone (**13**), 3-ethynyl-2-naphthaldehyde (**14**) and naphthocyclopentadienone (**15**). The mechanism for the formation of **13-15** is proposed to involve double migrations of the benzoate group into the isonaphthofuran ring.
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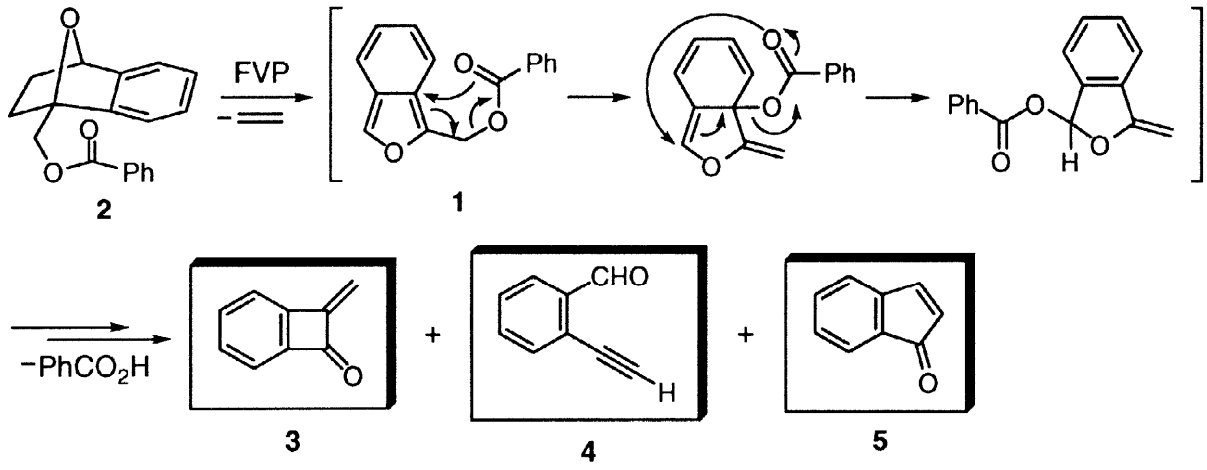
Recently, we have reported that pyrolysis of (1-isobenzofuryl)methyl benzoate (**1**), produced in situ from flash vacuum pyrolysis (FVP) of (7-oxa-1-benzonorbornenyl)methyl benzoate (**2**), gives methylenecyclobutenone (**3**), ethynylbenzaldehyde (**4**) and benzocyclopentadienone (**5**) as the major products.[1] The mechanism for the formation of **3-5** is proposed to involve double migrations of the benzoate group into the isobenzofuran ring (Scheme 1).



Scheme 1

The novelty of the chemistry of **1** prompted us to extend our study to its isonaphthofuran analogue, (1-isonaphthofuryl)methyl benzoate (**6**). We report here the results of this investigation.

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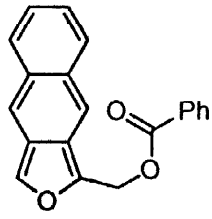
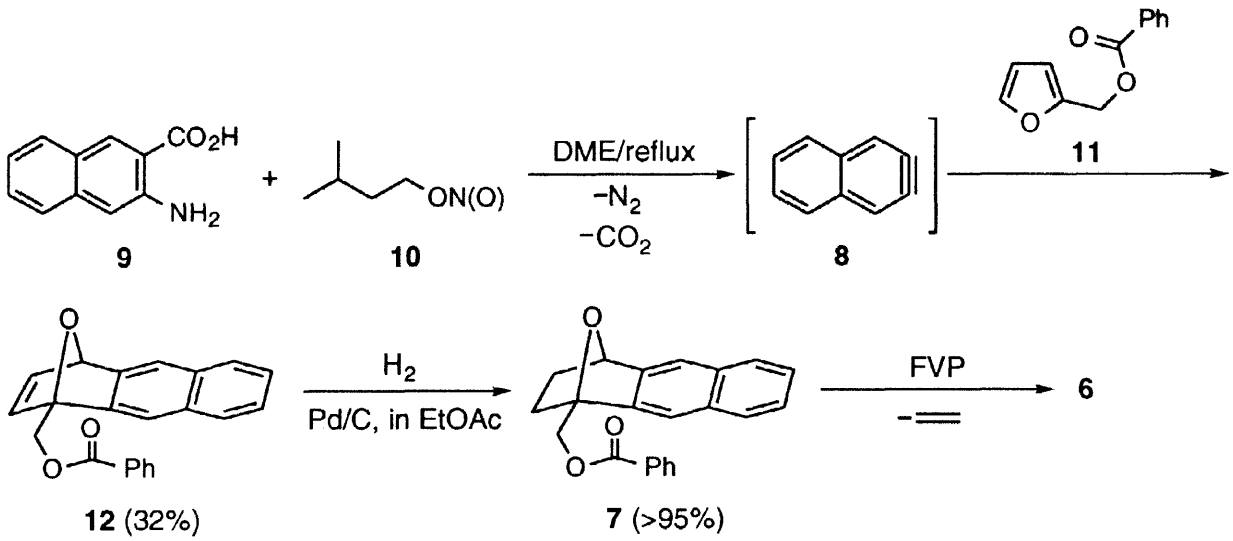


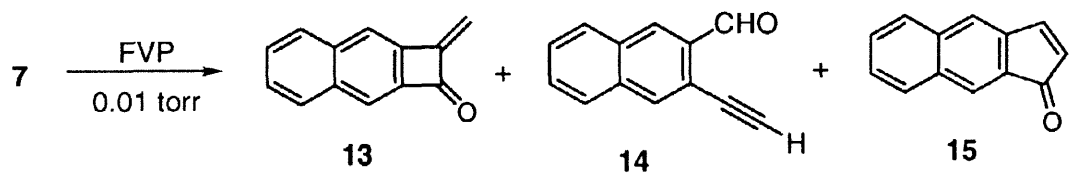
6

Due to the high reactivity of the isonaphthofuran system, **6** was generated as a reaction intermediate from retro Diels-Alder reaction of (7-oxa-1-naphthonorbornenyl)methyl benzoate (**7**) by the pyrolysis method. Synthesis of the precursor **7** is outlined in Scheme 2. Treatment of 2,3-didehydronaphthalene (**8**), produced in situ by reaction of 3-amino-2-naphthoic acid (**9**) with isoamyl nitrite (**10**) in refluxing 1,2-dimethoxyethane (DME),[2] with (2-furyl)methyl benzoate (**11**)[3,4] gave the Diels-Alder product (7-oxa-1-naphthonorbornadienyl)methyl benzoate (**12**).[5] Hydrogenation of **12** over Pd/C then led to **7**.[6]

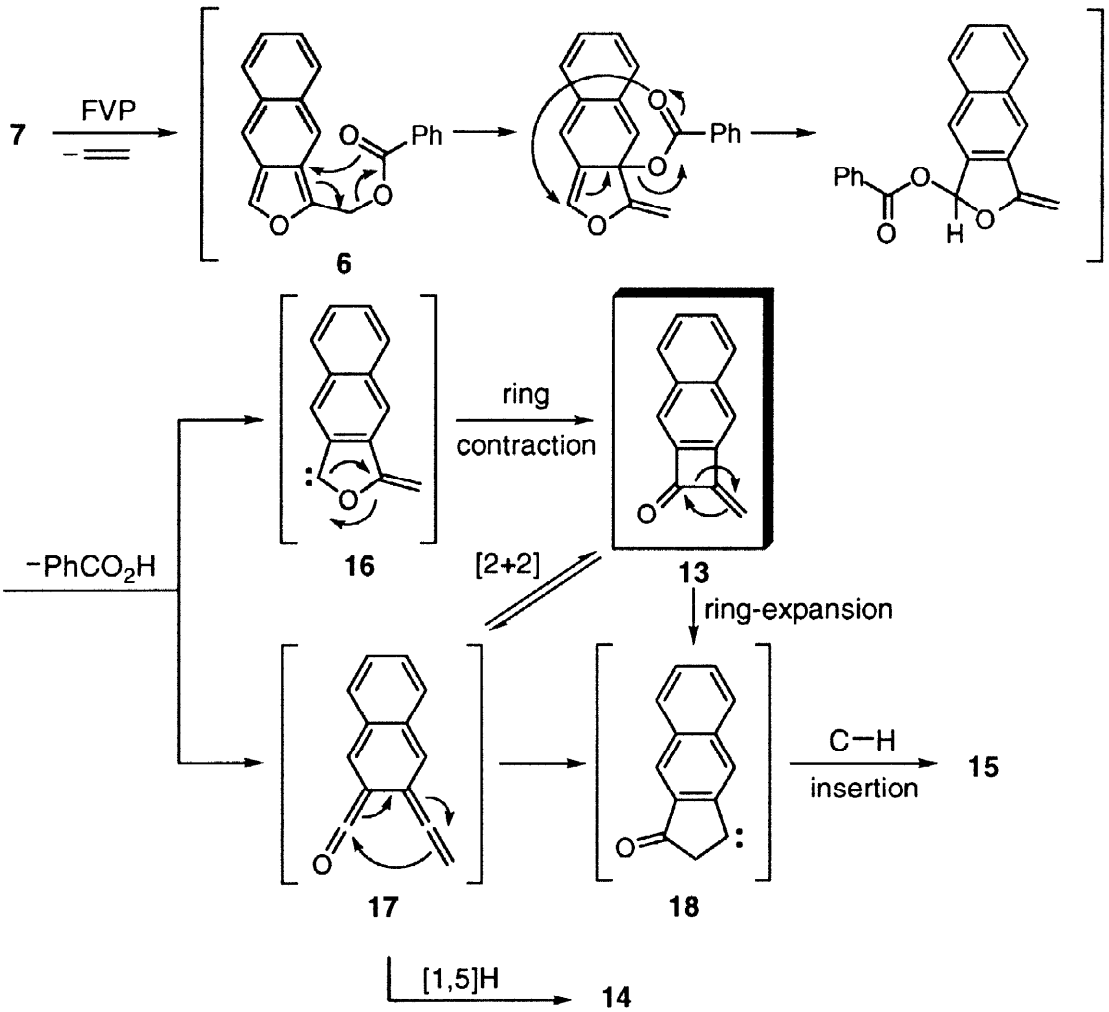


Scheme 2

FVP of **7** was performed at temperatures at 550°C and ca. 10^{-2} torr by using the previously reported method.[7] and gave methylenenaphthocyclobutenone (**13**),[8] 3-ethynyl-2-naphthaldehyde (**14**)[9] and naphthocyclopentadienone (**15**)[10,11] as the major products. When the pyrolysis temperature was raised to 700°C, **15** was obtained as the sole product. The proposed mechanism for the formation of **13-15** is presented in Scheme 3.



550 °C	48%	9%	28%
700 °C	—	—	65%



Scheme 3

Similar to the pyrolytic chemistry of **1**, the benzoate group in (1-isonaphthofuryl)methyl benzoate (**6**), generated via a retro Diels-Alder reaction of **7**, underwent double migrations into the isonaphthofuran ring and a subsequent α-elimination gave the carbene intermediate **16** or allene-ketene **17**. Compound **13** could be produced either from carbene **16** via a ring-contraction process or from **17** via an intramolecular [2+2] reaction. Ring-expansion of **13** or ring-closure of **17** could give carbene intermediate **18**, which can undergo a C-H insertion reaction to give **15**. Finally, a 1,5-H shift of **17** gave **14**.

Further work to prepare the derivatives of **6** and to study their pyrolytic chemistry by the present methodology is in progress.

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References and Notes

1. Chen, P.S.; Chou, C.H. *Tetrahedron* **1997**, *53*, 17115.
2. Friedman, L.; Logullo, F.M. *J. Org. Chem.* **1969**, *34*, 3089.
3. Trahanovsky, W.S.; Park, M.-G. *J. Am. Chem. Soc.* **1973**, *95*, 5412.
4. Trahanovsky, W.S.; Park, M.-G. *J. Org. Chem.* **1974**, *39*, 1448.
5. **12**: mp=150-151 °C; IR (KBr, cm^{-1}) 3050-2950, 1715; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.11-8.08 (m, 2H), 7.74-7.71 (m, 2H), 7.60-7.54 (m, 3H), 7.46-7.41 (m, 4H), 7.06-7.03 (m, 1H), 6.90-6.88 (m, 1H), 5.85 (s, 1H), 5.36 (d, J=12.6 Hz, 1H), 5.12 (d, J=12.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.47, 145.01, 143.42, 143.37, 140.89, 133.25, 131.82, 131.71, 129.86, 129.59, 128.42, 128.26, 128.06, 126.39, 126.29, 118.70, 118.05, 90.51, 81.86, 61.88; MS (LR, 70 eV) m/z (%) 328 (M^+, 11), 181 (21), 178 (57), 165 (59), 163 (43), 152 (23), 106 (22), 105 (100), 77 (80), 51 (16); Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91. Found: C, 80.22; H, 4.94.
6. **7**: mp=154-155 °C; IR (KBr, cm^{-1}) 3050-2950, 1725; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.07-8.04 (m, 2H), 7.82-7.79 (m, 2H), 7.64-7.63 (m, 2H), 7.55-7.36 (m, 5H), 5.55 (d, J=5.1 Hz, 1H), 5.16 (s, 2H), 2.33-2.28 (m, 1H), 2.16-2.10 (m, 1H), 1.62-1.59 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.45, 144.13, 142.77, 133.08, 132.81, 132.63, 129.76, 129.70, 128.34, 128.26, 128.07, 125.85, 125.73, 117.10, 116.40, 86.65, 78.91, 63.21, 29.39, 29.23; MS (LR, 70 eV) m/z (%) 330 (M^+, 11), 303 (22), 302 (86), 197 (17), 181 (100), 165 (29), 152 (45), 105 (65), 77 (63), 51 (14); HRMS Calcd for $C_{22}H_{18}O_3$: 330.1256. Found: 330.1247; Anal. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 79.65; H, 5.47.
7. Chou, C.H.; Trahanovsky, W.S. *J. Am. Chem. Soc.* **1986**, *108*, 4138.
8. **13**: IR (KBr, cm^{-1}) 1760, 1588; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.96-7.85 (m, 4H), 7.62-7.48 (m, 2H), 5.67 (d, J=0.9 Hz, 1H), 5.44 (d, J=0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 186.98, 156.39, 152.37, 150.77, 137.17, 134.29, 130.70, 129.03, 127.14, 121.03, 118.12, 105.03; GC-MS (LR, 70 eV) m/z (%) 180 (M^+, 55), 152 (100), 151 (31), 126 (10), 76 (15).
9. **14**: ^1H NMR ($CDCl_3$, 300 MHz) δ 10.61 (s, 1H), 8.0–7.4 (m, 6H), 3.47 (s, 1H). GC/MS (LR, 70ev) m/z (%) 180 (M^+, 58), 152 (100), 151 (29), 76 (22), 63 (18), 44 (33).
10. Morris, J.L.; Becker, C.L.; Fronczek, F.R.; Daly, W.H.; Mclaughlin, M.L. *J. Org. Chem.* **1994**, *59*, 6484.
11. **15**: mp=154-155 °C; IR (KBr, cm^{-1}) 1700, 1625.^1H NMR ($CDCl_3$, 300 MHz) δ 7.89 (s, 1H), 7.85-7.72 (m, 3H), 7.52-7.45 (m, 2H), 7.38 (s, 1H), 6.14 (d, J=5.7 Hz, 1H) [lit.[9] ^1H NMR ($CDCl_3$, 200 MHz) δ 7.95-7.30 (m, 7H), 6.14-6.11 (d, 1H)]; ^{13}C NMR ($CDCl_3$, 75 MHz) : δ 196.93, 150.40, 139.52, 136.11, 133.65, 131.12, 130.89, 129.75, 129.08, 128.79, 127.19, 124.16, 121.73; GC-MS (LR, 70 ev) : 181 (M^++1, 15), 180 (M^+, 100), 152 (58), 151 (21), 126 (15), 76 (12) [lit.[9] GC-MS m/z 180]; HRMS Calcd for $C_{13}H_8O$: 180.0575. Found : 180.0577.