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The High-Temperature Gas-Phase Reactions of *o*-Allylbenzyl Radicals Generated by Flash Vacuum Pyrolysis of Bis(*o*-allylbenzyl) Oxalate

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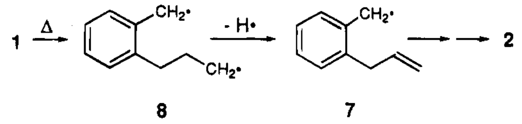
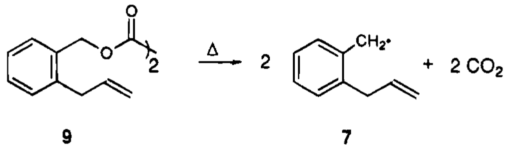
In the gas-phase thermal decomposition of tetralin (**1**),[1,2] the major products include 1,2-dihydronaphthalene (**2**) and naphthalene (**3**), derived by the loss of hydrogen, and benzocyclobutene (**4**) and styrene (**5**), derived by the loss of ethylene (Scheme 1). Several other significant products such as indene (**6**), formed by the loss of the equivalent of methane from **1**, are also produced. One of the mechanisms proposed[2l] for the formation of **2** involves the *o*-allylbenzyl radical (**7**) formed from diradical **8** by loss of a hydrogen atom. Conversion of **7** to **2** is reasonable, but previous studies[3] of related radicals indicate that **7** could produce other products such as **6**. In an attempt to determine the fate of radical **7** under high-temperature gas-phase conditions, we have studied the flash vacuum pyrolysis (FVP) of bis(*o*-allylbenzyl) oxalate (**9**). Oxalates have been shown to be good precursors of benzyl radicals under FVP conditions[4] and we expected **9** to produce **7** in good yield.

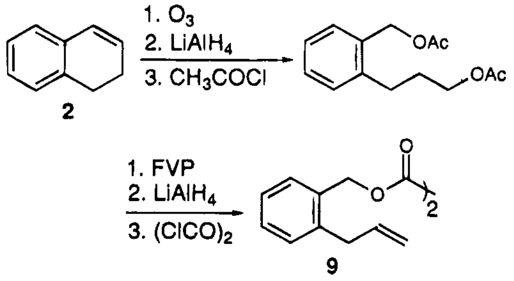




The results of the study of the FVP of **9** are presented in this Note.

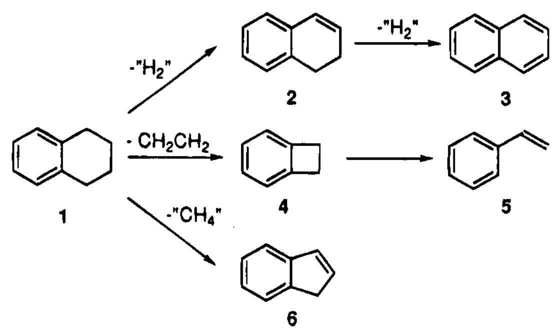
Results

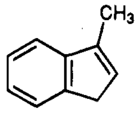
Oxalate **9** was prepared from 1,2-dihydronaphthalene (**2**) by the following reaction sequence.



The FVP of **9** (Table 1) leads primarily to the formation of 1,2-dihydronaphthalene (**2**), naphthalene (**3**), indene (**6**), and 3-methyl-1*H*-indene (**10**). Small amounts (<2% at 700 °C) of 2-methyl-1*H*-indene (**11**), tetralin (**1**), *o*-allyltoluene (**12**), and 1,4-dihydronaphthalene (**13**) were produced. 1,2-Bis(*o*-allylphenyl)ethane (**14**) was detected (<1%) at 700−750 °C.

Scheme 1





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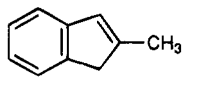

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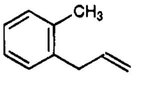

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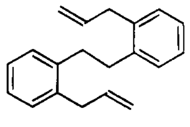

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Discussion

Previous work in this laboratory has shown that the FVP of bis oxalate esters produces high yields of benzyl radicals.[4] The formation of *o*-allylbenzyl radical (**7**) in the pyrolysis of bis(*o*-allylbenzyl) oxalate (**9**) is confirmed by the production at lower pyrolysis temperatures of 1,2-bis(*o*-allylphenyl)ethane (**14**), the dimer of radical **7**.

The gas-phase chemistry of radical **7** and other related radicals (Scheme 2), such as 1-tetryl (**15**), 2-tetryl (**16**), 1-indanylmethyl (**17**), and 2-indanylmethyl (**18**), have

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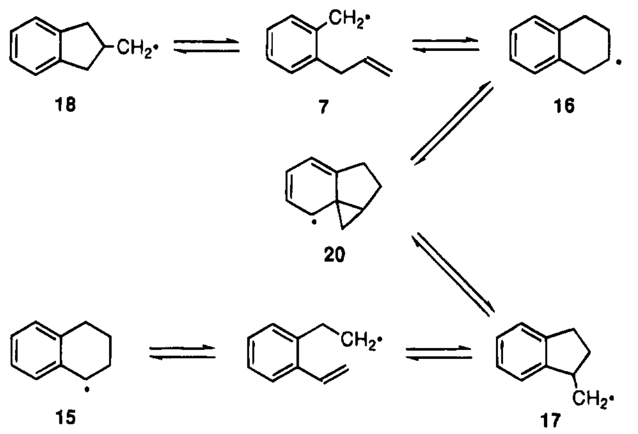
Table 1. Products and Recovered Starting Material from FVP of Bis(*o*-allylbenzyl) Oxalate (9) at Various Oven Temperatures[a,b]

	yield, %[c]				
entry	700 °C	750 °C	800 °C	850 °C	900 °C
bis(*o*-allylbenzyl) oxalate (**9**)	3.4	1.7	1.2	0.3	–
1,2-dihydronaphthalene (**2**)	62.6	62.2	60.5	55.2	46.4
naphthalene (**3**)	5.3	7.5	11.1	16.5	27.1
indene (**6**)	6.3	6.9	8.2	10.1	12.3
3-methyl-1*H*-indene (**10**)	4.2	4.4	3.6	2.9	2.2
2-methyl-1*H*-indene (**11**)	1.4	1.5	1.8	1.7	1.8
tetralin (**1**)	1.0	1.2	1.1	1.2	1.0
o-allyltoluene (**12**)	1.4	1.0	0.8	0.6	0.3
1,4-dihydronaphthalene (**13**)	1.6	1.0	0.4	0.2	–
1,2-di(*o*-allylphenyl)ethane (**14**)	0.7	0.2	–	–	–
other products	12.0[d]	12.3[d]	11.3[d]	11.2[d]	8.9[d]
recovery[e]	71.5	65.1	68.7	67.1	59.9
conversion[f]	96.6	98.3	98.8	99.7	100

[a] FVP conditions: system pressure = 1×10^{-5} torr, sample temperature = 60–80 °C. [b] Amounts determined by GC with a known quantity of triphenylmethane added as standard. Data represent the average of triplicate runs. [c] Moles of product divided by total moles of recovered material. [d] See Table S-I in the Supplementary Material for a more detailed analysis. Only products that were identified and produced in ≥1% yield at 700 °C and **14**, the dimer of **7**, are included in Table 1. [e] Total moles of recovered material divided by moles of starting material used. [f] Total moles of recovered material minus moles of recovered starting material divided by moles of recovered material.

Scheme 2



been studied;[3] although, the high-temperature gas-phase chemistry of **7** was not investigated directly.[3a,b] The thermal behavior of **7** is similar to that of 5-hexenyl radicals. There is a kinetic preference of *ca.* 2 kcal mol^{-1} for the formation of the less stable five-membered 2-indanylmethyl radical (**18**) over the six-membered 2-tetryl radical (**16**).[3c] However, under pyrolysis conditions, the initial closure will be reversible and the chemistry of the more stable **16** should predominate.

Consistent with this analysis, the FVP of bis oxalate ester **9** leads primarily to the formation of 1,2-dihydronaphthalene (**2**) produced by loss of one of the β hydrogens from **15** or **16**. Additionally, 1,4-dihydronaphthalene (**13**), produced by the loss of a β hydrogen from **16**, was also detected as a minor product. Significant amounts of naphthalene (**3**), from the secondary pyrolysis of **2**, were also observed. Products such as **10** and **11**, formed from radicals **17** and **18**, are consistent with Scheme 2 and the literature results.[3a,b,5]

The pyrolysis of oxalate **9** also produces a small amount of indene (**6**). Indene (**6**) was also detected in the previous study of radicals related to **7**[3a,b] and in the pyrolysis of tetralin (**1**). In order to evaluate radical **7** and related radicals as the source of indene **6** in the decomposition of **1**, a comparison of the data from the pyrolysis of **9** with comparable data from **1** was undertaken.

In the pyrolysis of tetralin (**1**), the ratio of indene (**6**) to dehydrogenation products **2** and **3** increases from 0.3 to 0.6 at 900–950 °C,[7] but in the pyrolysis of **9** the ratio of **6** to **2** and **3** is significantly lower. In the pyrolysis of **9** a maximum ratio of 0.17 at 900 °C was observed (Table 1). Therefore the major route to **6** in the decomposition of **1** cannot involve radical **7** since more **6** is produced from the thermal decomposition of **1** than can be accounted for with **7** as the source. Other recent work in our laboratory[7] indicates that the major source of **6** involves the pathway **1** to *o*-allyltoluene (**12**) to 2-methylindan (**19**) to **6**. In the pyrolysis of oxalate **9**, any of the radicals **17**, **18**, or **20** could be the source of **6**.

The minor products **1** and **12** are probably the result of bimolecular hydrogen abstraction by radicals **15** and **16**, and **7**, respectively. Some of the **12** formed may also be the result of the secondary pyrolysis of **1** at higher temperatures.

Conclusion

The results of the FVP of bis(*o*-allylbenzyl) oxalate (**9**) are consistent with the formation of *o*-allylbenzyl radical (**7**). The major product from **7** is 1,2-dihydronaphthalene (**2**) which is readily explained by closure of **7** to **16** followed by the loss of a β hydrogen atom. Other products which could come from radical **7** are formed in relatively low yields. Comparison of the pyrolysis products of **9** with those of tetralin (**1**) leads us to conclude that radical **7** is not a major source of indene (**6**) in the thermal decomposition of **1**.

Experimental Section

Methods and Materials. Some general methods have been described previously.[8] ^{1}H NMR spectra were recorded on a Nicolet NT-300 spectrometer. FTIR spectra were obtained on an IBM IR/98 spectrophotometer. GCMS were performed on a Finnegan 4000 mass spectrometer. All materials were commercially available and used as received, except where indicated. A Welsbach ozonator was used to generate a stream of ozone in oxygen.

Bis(*o*-allylbenzyl) Oxalate (9). 1,2-Dihydronaphthalene (2.6 g, 0.020 mol) was dissolved in CH_2Cl_2 (100 mL) and the solution was cooled to −78 °C. O_3 (*ca.* 2% in O_2) was bubbled through the solution until a blue color developed. Excess O_3 was then removed by bubbling N_2 through the solution until the blue color had dissipated. The reaction mixture was warmed to room temperature and the solvent was removed *in vacuo*. The ozonide was dissolved in THF (15 mL) and added dropwise to a slurry of $LiAlH_4$ (0.8 g, 0.022 mol) in THF (100 mL) at 0 °C. After the addition was complete, the reaction mixture was stirred overnight at room temperature. A slurry of wet Na_2SO_4 was added

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(5) Methylindenes **10** and **11** may interconvert by a series of 1,5 hydrogen and 1,5 methyl shifts at high temperatures.[6]

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to the reaction mixture until evolution of H_2 ceased. The white solid was filtered off and washed with ethyl acetate. The filtrate was dried ($MgSO_4$) and the solvent was removed *in vacuo*. The crude diol was distilled at 150 °C (0.2 torr) to yield *o*-(3-hydroxypropyl)benzyl alcohol (2.54 g, 0.015 mol, 75% yield): FTIR (thin film) 3375 (br), 2937, 1032, 758 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.33–7.14 (m, 4 H), 4.67 (s, 2 H), 3.50 (t, $J = 6.0$ Hz, 2 H), 2.82 (t, $J = 6.9$ Hz, 2 H), 1.90 (quintet, $J = 6.6$ Hz, 2 H).

o-(3-Hydroxypropyl)benzyl alcohol (3.0 g, 0.018 mol) was dissolved in dry ether (50 mL), and triethylamine (4.0 g, 0.040 mol, *ca.* 5.5 mL) was added. The mixture was cooled to 0 °C and a solution of acetyl chloride (3.1 g, 0.040 mol, *ca.* 2.8 mL) in ether (20 mL) was added dropwise. After the addition was complete, the reaction mixture was stirred for 10 min at 0 °C and then overnight at room temperature. The reaction mixture was washed with H_2O (20 mL), saturated $NaHCO_3$ (20 mL), and H_2O (20 mL) and then dried ($MgSO_4$). The solvent was removed *in vacuo* to yield *o*-(3-acetoxypropyl)benzyl acetate (4.1 g, 0.016 mol, 89% yield): FTIR (thin film) 2960, 1749, 1454, 1383, 1367, 1259, 1034, 758 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.37–7.18 (m, 4 H), 5.14 (s, 2 H), 4.11 (t, $J = 6.4$ Hz, 2 H), 2.74 (t, $J = 7.8$ Hz, 2 H), 2.11 (s, 3 H), 2.07 (s, 3 H), 2.01–1.90 (m, 2 H).

o-(3-Acetoxypropyl)benzyl acetate (3.9 g, 0.016 mol) was pyrolyzed at 700 °C and 1×10^{-5} torr with a sample temperature of 80 °C.[4c,8] The pyrolysate was dissolved in ether and treated with K_2CO_3. The solvent was removed *in vacuo* and the crude product was purified by flash chromatography on a silica gel column (50 × 150 mm) with 1:1 hexanes to CH_2Cl_2 to yield *o*-allylbenzyl acetate (1.5 g, 7.9 mmol, 49% yield): FTIR (thin film) 2924, 1742, 1229, 1026, 754 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.37–7.18 (m, 4 H), 5.96 (ddt, $J_d = 16.8$ Hz, $J_d = 10.3$ Hz, $J_t = 6.3$ Hz, 1 H), 5.07 (dd, $J_d = 10.2$ Hz, $J_d = 1.1$ Hz, 1 H), 4.99 (dd, $J_d = 17.1$ Hz, $J_d = 1.1$ Hz, 1 H), 5.13 (s, 2 H), 3.44 (d, $J = 6.2$ Hz, 2 H), 2.09 (s, 3 H).

o-Allylbenzyl acetate (1.5 g, 7.9 mmol) was dissolved in THF (10 mL) and added dropwise to a slurry of $LiAlH_4$ (0.4 g, 0.010 mol) in THF (50 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. A slurry of wet Na_2SO_4 was added to the reaction mixture until evolution of H_2 ceased. The white solid was filtered off and washed with ethyl acetate. The filtrate was dried ($MgSO_4$) and the solvent was removed *in vacuo* to yield *o*-allylbenzyl alcohol (1.1 g, 7.4 mmol, 94% yield): FTIR (thin film) 3333 (br), 2918, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.41–7.36 (m, 1 H), 7.34–7.18 (m, 3 H), 6.01 (ddt, $J_d = 16.8$ Hz, $J_d = 10.4$ Hz, $J_t = 6.3$ Hz, 1 H), 5.07 (dq, $J_d = 10.1$ Hz, $J_q = 1.5$ Hz, 1 H), 5.00 (dd, $J_d = 17.2$ Hz, $J_d = 1.5$ Hz, 1 H), 4.71 (d, $J = 5.9$ Hz, 2 H), 3.48 (dt, $J_d = 6.2$ Hz, $J_t = 1.4$ Hz, 2 H), 1.26 (t, $J = 6.0$ Hz, 1 H) [lit.[3c] ^1H NMR ($CDCl_3$) δ 7.6–7.1 (m, 4 H), 6.02 (ddt, $J_d = 16.6$ Hz, $J_d = 10.5$ Hz, $J_t = 6.1$ Hz, 1 H), 5.05 (m, 1 H (*cis*)), 5.0 (m, 1 H (*trans*)), 4.70 (s, 2 H), 3.47 (dt, 2 H), 1.6 (s, 1 H)].

o-Allylbenzyl alcohol (1.2 g, 8.0 mmol) was dissolved in ether (150 mL), and triethylamine (1.1 g, 0.011 mol) was added. The reaction mixture was cooled to 0 °C and oxalyl chloride (0.8 g, 6.0 mmol) in ether (10 mL) was added dropwise. After the reaction mixture was stirred for 1 h at room temperature, it was extracted with H_2O (50 mL), saturated $NaHCO_3$ (2 × 50 mL), H_2O (50 mL), and saturated NaCl (50 mL) and then dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude product was purified by flash chromatography on a silica gel column (30 × 150 mm) with 1:1 CH_2Cl_2 to hexanes to yield bis(*o*-allylbenzyl) oxalate (1.1 g, 3.2 mmol, 80% yield). FTIR (thin film) 2957, 2924, 1767, 1744, 1155 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.41–7.19 (m, 4 H), 5.94 (ddt, $J_d = 16.8$ Hz, $J_d = 10.4$ Hz, $J_t = 6.3$ Hz, 1 H), 5.33 (s, 2 H), 5.02 (dq, $J_d = 10.1$ Hz, $J_q = 1.5$ Hz, 1 H), 4.95 (dd, $J_d = 17.0$ Hz, $J_d = 1.7$ Hz, 1 H), 3.45 (dt, $J_d = 6.2$ Hz, $J_t = 1.4$ Hz, 2 H); GCMS (CI, NH_3) *m/e* 368 (M + NH_4); GCMS (EI, 70 eV) *m/e* (% base peak) 260 (5.5), 219 (4.8), 131 (100), 130 (98.6), 116 (15.6), 115 (22.0), 91 (45.6). Anal. Calcd for $C_{22}H_{22}O_4$: C, 75.41%; H, 6.33%. Found: C, 75.42%; H, 6.36%.

Flash Vacuum Pyrolysis. Flash vacuum pyrolysis (FVP) was performed as previously described.[4c,9]

Product Analysis. FVP reaction mixtures were analyzed by capillary gas chromatography on a Hewlett-Packard HP5840A gas chromatograph equipped with a 30-m (0.25-μm film thickness) DB-1701 capillary column. Major products were identified by comparison of their GC retention times to those of authentic samples (**1–6**, **9–12**, **19**, toluene, ethylbenzene, *o*-xylene, *o*-ethyltoluene, and 1-methylindan) and GCMS. The molecular weight of minor products was determined by GCMS. The major products (**1–6**, **9**, **12**, toluene, ethylbenzene, *o*-xylene, and *o*-ethyltoluene) were corrected for FID response to a known amount of added standard (triphenylmethane). A more detailed analytical procedure is described elsewhere.[7]

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-7405-ENG-82.

Supplementary Material Available: Detailed product analysis from the FVP of **9** (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(9) Commercial apparatus is available from Kontes Scientific Glassware, Vineland, NJ 08360. For review, see Brown, R. C. F. *Pyrolysis Methods in Organic Chemistry*; Academic: New York, 1980; Chapter 2.