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ORGANIC OXALATES. III. CYCLIZATIONS OF THE CINNAMYL RADICAL TO FORM INDENE AND THE ORTHO-PHENYLBENZYL RADICAL TO FORM FLUORENE (1)*

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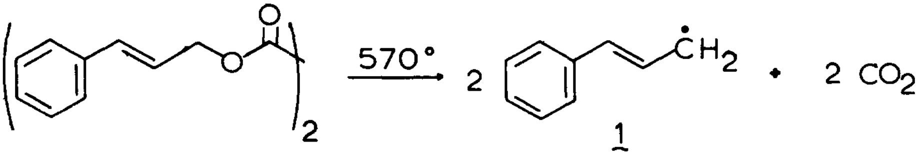
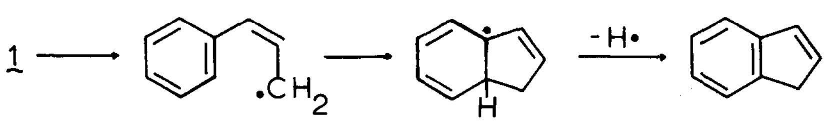
Recently we reported that low-pressure gas-phase pyrolysis of organic oxalates offers a convenient means of generating relatively stable radicals, such as benzyl radicals, in the absence of any very reactive radicals or molecules (1). We now wish to report that the cinnamyl and ortho-phenylbenzyl radicals generated from the appropriate oxalate undergo internal cyclization reactions to form indene and fluorene respectively.





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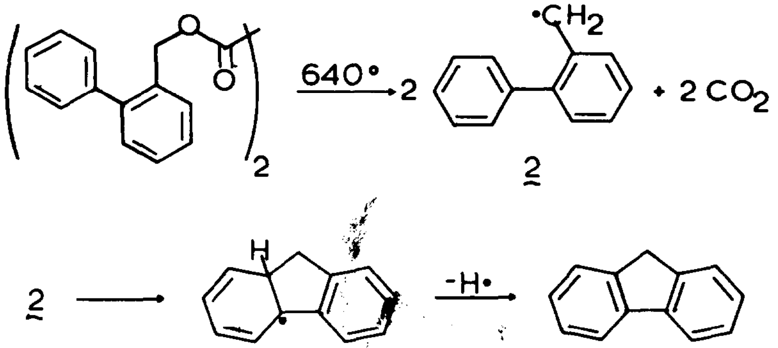
* Based on work by C. C. Ong in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Iowa State University.



trans-Cinnamyl oxalate was prepared in 70% yield from cinnamyl alcohol and oxalyl chloride in the presence of triethylamine (1). Recrystallization of the oxalate from 95% ethanol gave white crystals, mp 102-104°, ir (CHCl$_3$) 1770,1740 cm^{-1}(C=O);nmr(CDCl$_3$) δ 7.27 (m, 10), 6.4 (m, 4), and 4.88 (d, 4, J = 6 Hz).

Anal.** Calcd for $C_{20}H_{18}O_4$: C, 74.50; H, 5.63. Found: C, 74.51; H, 5.44.

trans-Cinnamyl oxalate was pyrolyzed in the gas phase at 570° using the previously described apparatus (1). A known amount of methyl oxalate was added to the pyrolysate as an internal standard. The characteristic nmr spectrum of indene was the main feature of the nmr spectrum of the pyrolysate and integration of its methylene group and the methyl signal for methyl oxalate showed that 0.82 mole of indene per mole of oxalate was produced. Glpc analysis of the pyrolysate showed that per mole of oxalate 0.19 mole of styrene, 0.11 mole of trans-β-methylstyrene, 0.098 mole of allylbenzene, 0.014 mole of toluene, small amounts of two unknown products and no indane were produced in addition to the indene. Pyrolysis of the oxalate at 650° gave very similar yields of products with the amount of indene being 0.86 mole per mole of oxalate.

** Analyzed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

ortho-Phenylbenzyl oxalate was prepared in 73% yield from ortho-phenylbenzyl alcohol and oxalyl chloride in the presence of triethylamine (1). Recrystallization of the oxalate from 95% ethanol gave white crystals, mp 108-110°, ir ($CHCl_3$) 1775, 1752 cm^{-1} (C=O); nmr($CDCl_3$) δ 7.31 (broad s, 18) and 5.2 (s, 4).

Anal.** Calcd for $C_{28}H_{22}O_4$: C, 79.59; H, 5.25. Found: C, 79.55; H, 5.22.

Pyrolysis of o-phenylbenzyl oxalate at 640° gave 1.44 moles of fluorene and 0.025 mole of ortho-phenyltoluene per mole of oxalate based on glpc analysis using bibenzyl as an internal standard. The yield of fluorene was further confirmed by nmr analysis using benzyl sulfide as an internal standard.

All of the products obtained from the pyrolysis of trans-cinnamyl oxalate can readily be interpreted as coming from the cinnamyl radical. The cinnamyl radical has been generated by the decomposition of acetyl peroxide in allylbenzene (2) and the thermal decomposition of t-butylperoxy 2-phenyl-3-butenoate and t-butylperoxy 4-phenyl-3-butenoate in chlorobenzene (3). Under these conditions, low yields of the products from the coupling of cinnamyl radicals and no indene was obtained. It is most likely that any indene formed under these conditions would have been destroyed by reaction with the relatively unstable alkoxy radicals that were present. Large amounts of polymeric material were reported in both cases.

Removal of the hydrogen atom from the cyclized radicals deserves some consideration, since the amounts of unsaturated cyclized products, especially in the case of fluorene are quite high. A reasonable explanation for loss of so much hydrogen is transfer to organic material that is deposited on the pyrolysis column. Even a small amount of polymeric material could pick up quite a large number of hydrogen atoms. The driving force for hydrogen atom donation from the cyclized radicals must be formation of the conjugated systems.

Study of the pyrolyses of substituted cinnamyl and *ortho*-phenylbenzyl oxalates is in progress.

Acknowledgement

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