

Organic Oxalates. Cyclizations of the *ortho*-Methyl- and *ortho*-Trifluoromethyl-cinnamyl Radicals to the Corresponding Indenes¹

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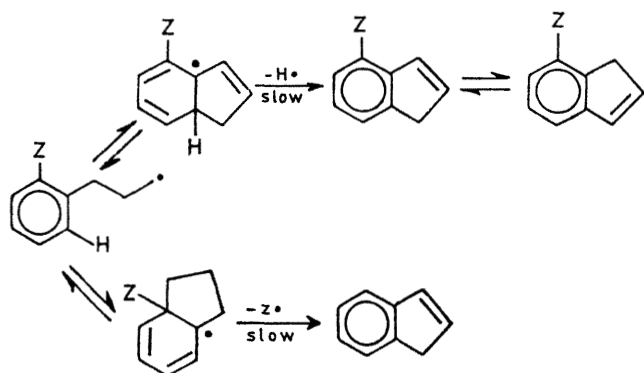
Summary *ortho*-Methyl- and *ortho*-trifluoromethyl-cinnamyl radicals, generated by gas-phase pyrolysis of the appropriate oxalate, undergo cyclization reactions to form indene or substituted indenenes.

WE have recently reported that the cinnamyl radical, generated by the gas-phase pyrolysis of dicinnamyl oxalate, undergoes a cyclization reaction to form indene in very good yield.^{1,2} We have also observed an isotope effect,

k_H/k_D , of 2.92 for the cyclization of *o*-deuteriocinnamyl radical to indene, which suggests that formation of the intermediate cyclic radical from the cinnamyl radical is a reversible step.¹ Thus, the cyclization of an *ortho*-substituted cinnamyl radical could lead to indene or a substituted indene by the mechanism shown in Scheme 1. The exact nature of the last step is not known and could involve the transfer of the radical to another species or unimolecular ejection of the radical.³ A similar scheme,

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involving two competing reactions, can be drawn for *meta*-substituted cinnamyl radicals. We have initiated a study of the cyclization of substituted cinnamyl radicals



SCHEME 1

in order to determine the effects of substituents on the two cyclization pathways. By studying the cyclization of the *o*-methyl- and *o*-trifluoromethyl-cinnamyl radicals, we had hoped to determine whether the electronic nature of the substituent, in the absence of a varying steric effect, would cause the relative rates of formation of indene to substituted indenenes to change. The striking differences in the relative rates of the two cyclization pathways of these two cinnamyl radicals has prompted us to communicate these results.

o-Bromotoluene and acraldehyde were converted into 1-*o*-methylphenylallyl alcohol by the method of Ouellette, Robins, and South.⁴ This alcohol was converted into the oxalate, which was rearranged to di-*o*-methylcinnamyl oxalate by heating to 220° for a few mins, m.p. 88–89°.‡

o-Bromotrifluoromethylbenzene and acraldehyde were converted into 1-*o*-trifluoromethylphenylallyl alcohol by the method used for the methyl compound.⁴ The alcohol resisted the acid-catalysed rearrangement that is normal for 1-arylallyl alcohols.⁵ The unrearranged alcohol was converted into the corresponding oxalate, which was purified by three successive high-vacuum molecular distillations, b.p. 95–110° (10⁻⁵ mm Hg).‡

The oxalates were pyrolysed at 570–580° at 10⁻⁵ mm Hg pressure with a head temperature of 80–120°.§

The pyrolysis products from the di-*o*-methylcinnamyl oxalate were analysed by g.l.c. using a 20 ft. × 1/4 in. 20% SE-30 on Chromosorb P column at 175° and mesitylene or biphenyl as an internal standard. The material responsible for the g.l.c. peak assigned to indene was collected and shown by n.m.r. and mass-spectral analysis to be indene. The 4- and 7-methylindenenes were not completely separated from 1,2-dihydronaphthalene, so the three compounds were collected together and the mixture was analysed by n.m.r.

‡ The n.m.r. spectrum and elemental analysis of this compound were consistent with the assigned structure.

§ The pyrolysis apparatus will be described later and is similar to the one used before,¹ but can operate at lower pressures.

¹ Previous paper: W. S. Trahanovsky and C. C. Ong, *J. Amer. Chem. Soc.*, 1970, **92**, 7174.

² W. S. Trahanovsky and C. C. Ong, *Tetrahedron Letters*, 1968, 3627.

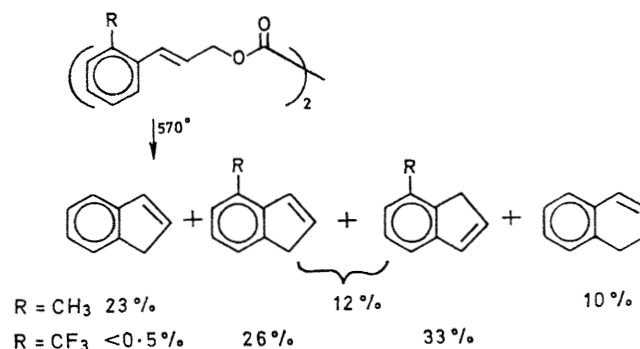
³ W. A. Pryor, J. P. Stanley, and M. G. Griffith, *Science*, 1970, **169**, 181.

⁴ R. J. Ouellette, R. D. Robins, and A. South, jun., *J. Amer. Chem. Soc.*, 1968, **90**, 1619.

⁵ Y. Pocker and M. J. Hill, *J. Amer. Chem. Soc.*, 1969, **91**, 3243.

⁶ (a) E. R. Morris and J. C. J. Thynne, *J. Organometallic Chem.*, 1969, **17**, P3; (b) G. O. Pritchard, G. H. Miller, and J. K. Foote, *Canad. J. Chem.*, 1962, **40**, 1830; (c) R. E. Dodd and J. W. Smith, *J. Chem. Soc.*, 1957, 1465; (d) G. O. Pritchard, H. O. Pritchard, H. I. Schiff, and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, 1956, **52**, 849; (e) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, 1966, p. 155.

and mass-spectral analysis. These products were the major ones, and their yields, based on two runs, are shown in Scheme 2.



SCHEME 2

The pyrolysis products from the di-1-(*o*-trifluoromethylphenyl)allyl oxalate were analysed by g.l.c. using a 13 ft. × 1/4 in. 20% DEGS on Chromosorb P column with mesitylene as a standard or a 20 ft. × 1/4 in. 20% SE-30 on Chromosorb P column with *m*-xylene as a standard. N.m.r. analysis of the product mixture using isobutyl methyl ketone as a standard gave results consistent with the g.l.c. analysis. No indene was detected in the product mixture and the lower limit of detection was <0.5%. The 4- and 7-trifluoromethylindenenes gave separate g.l.c. peaks using the DEGS column and were easily collected. Their structures were determined by mass-spectral and ¹H and ¹⁹F n.m.r. analysis. The two trifluoromethylindenenes were the only major products and their yields based on three runs are given in Scheme 2.

Thus, the (indene)/(substituted indenenes) ratio obtained from the di-*o*-methylcinnamyl oxalate was 2.0 and that obtained from the di-1-(*o*-trifluoromethylphenyl)allyl oxalate was <0.008. This large difference is most likely a result of the much slower loss of the trifluoromethyl radical than of the methyl radical in the last step of the formation of indene as given in Scheme 1. That the trifluoromethyl radical is less stable than the methyl radical is generally accepted from relative formation and hydrogen abstraction rates.⁶ Of course, polar character may develop in the bond that is breaking in the transition state of the fragmentation leading to indene. This polar effect could cause the trifluoromethyl group to cleave much more slowly than the methyl group. In any case, our results clearly show that the cinnamyl radical cyclization is very sensitive to the nature of the ring substituents.

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