

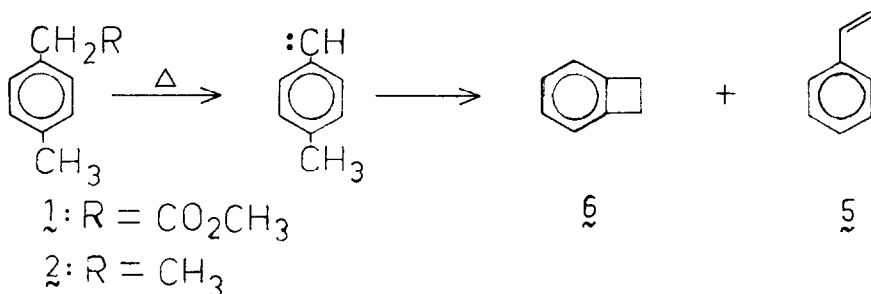
p-TOLYL CARBENE FROM METHYL p-TOLYLACETATE AND p-ETHYLTOLUENE¹

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Aryl³⁻⁹ and diaryl carbenes^{6,10} have recently been shown to undergo a remarkable series of interconversions when generated in the gas phase at high temperatures (> 250°).¹¹ In particular, when phenylcarbene is substituted with a remote methyl group, the resulting rearrangement to lower energy carbenes can be detected through the formation of styrene and benzocyclobutene.^{3,7,9} We report the successful utilization of such a process as a mechanistic probe in proving the intermediacy of p-tolylcarbene in the gas-phase pyrolysis of methyl p-tolylacetate(1)^{12,13} and p-ethyltoluene(2).



Pyrolyses were conducted by evaporating starting material at 0.2 torr into a quartz tube packed with quartz chips. Products were trapped in a receiver cooled by a Dry-Ice acetone slurry. Analysis of the condensate by VPC revealed the formation of toluene(3), p-xylene(4), styrene(5), benzocyclobutene(6),¹⁴ p-ethyltoluene(2) and p-methylstyrene(7) in various yields as the only hydrocarbon products (see Table 1).¹⁵ In the pyrolyses of (1), besides the hydrocarbon products, the starting methyl ester was also recovered in yields of 37.9, 68.3 and 100% at temperatures of 875, 810 and 750° C respectively.

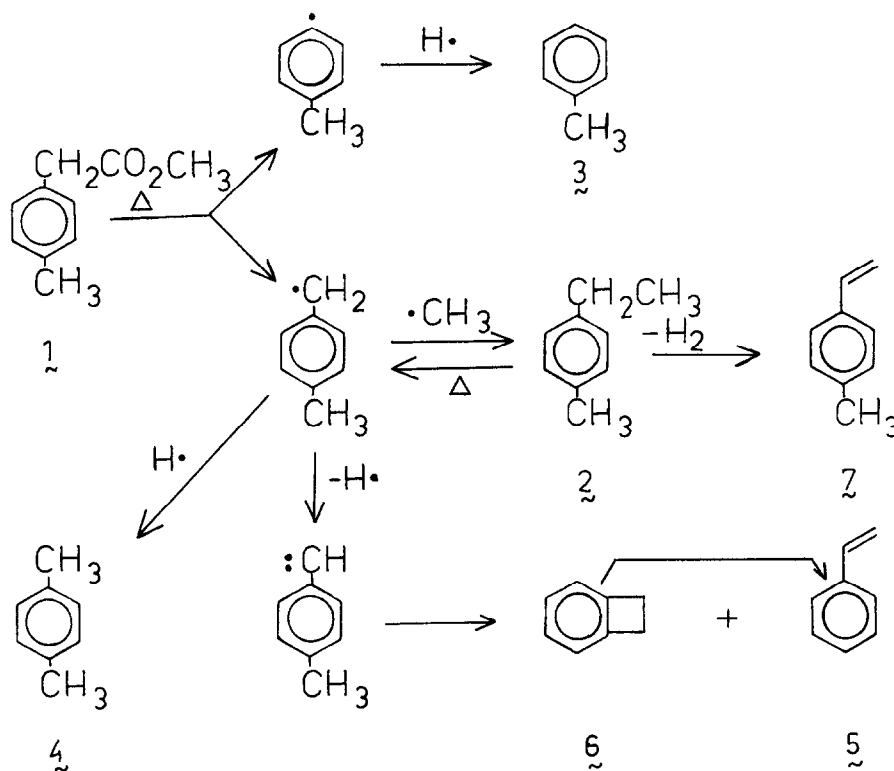
The results can best be explained in terms of two competitive fragmentation paths, a radical route resulting in the formation of 2, 3, 4, and 7 and a carbene path yielding 5 and 6 (see Scheme).^{16,17} It is the latter path which we sought in order to detect a mechanism

originally postulated in 1938 by Hurd and Blunck,¹⁸ who pyrolyzed methyl phenylacetate at 625°. A competitive carbene fragmentation with concurrent diarylcarbene rearrangement has also been observed by Lehr and Wilson¹⁹ in the pyrolysis of diaryloxalates.²⁰

Correcting for the styrene which is formed due to fragmentation of benzocyclobutene under the reaction conditions (see Table 1), the relative amounts of 6 and 5 formed from 1 at 875° and 810° are 41/59 and 39/61 respectively. These values are in agreement with those obtained from the pyrolysis of *p*-tolylidiazomethane³ at 420° (45/55) and thus consistent with the postulated intermediacy of *p*-tolylcarbene.

Methylene has been postulated as an intermediate in the pyrolytic "cracking" of hydrocarbons, but firm evidence for carbenes is lacking.²¹ We believe that the formation of styrene and benzocyclobutene upon pyrolysis of 2 is the first conclusive evidence for the intermediacy of carbenes in the thermolysis of aromatic hydrocarbons. It is unfortunate that at temperatures below 925°, where benzocyclobutene survives, the fragmentation to *p*-tolylcarbene is less significant and trace amounts of benzocyclobutene are not seen.

SCHEME



T A B L E 1
HYDROCARBON PRODUCT DISTRIBUTIONS^a

Starting Material	Temperature ^b (°C)	p-Methylstyrene (7)	p-Ethyltoluene (2)	Benzo-cyclo-butene (6)	Styrene (5)	p-Xylene (4)	Toluene (3)
Methyl	925	10.4(5.4)	62.6(31.9)	-	5.7(3.4)	18.0(10.6)	3.3(2.1)
p-Tolyl-	875	4.2(1.7)	77.1(30.3)	0.5(0.2)	3.9(1.7)	12.6(5.6)	1.7(0.8)
acetate	810	3.8(0.7)	71.0(13.9)	1.3(0.4)	4.1(0.9)	18.5(4.1)	1.3(0.3)
(1)	750	-	-	-	-	-	-
p-Ethyl-	925	29.2	24.1		9.5	26.5	10.7
toluene	875	19.1	56.0		2.2	17.7	5.0
(2)	810	7.7	85.8		trace	5.4	1.1
	750	-	100		-	-	-
Benzo-	925			5.7	94.3		
cyclo-	875			28.6	71.4		
butene	810			63.1	36.9		
(6)							
p-Xylene	925					95.3	4.7
(4)							
p-Methyl-	925	95.9			2.1		3.0
styrene							
(7)							
Ethyl-	925				22.9	Ethylbenzene 61.7	15.4
benzene							

^a Absolute yields (in parentheses) were determined using tert-butylbenzene as an internal VPC standard. The average of three runs was taken.

^b Temperatures were determined using a chromel-alumel thermocouple prior to filling a 14 x 200 mm quartz tube with quartz chips.

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1. Support of this work by the National Science Foundation through Grant GP-30797X and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is acknowledged with appreciation. We also wish to acknowledge Professor Maitland Jones, Jr., for support of this work and comments on the manuscript and Professor W. Kirmse for critically reading the final manuscript.
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(b) Petroleum Research Fellow 1971-72.
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