The Pyrolysis of Bis[phenyl(*p*-tolyl)methyl] Oxalate: Competing Fragmentation to Radicals and Carbenes

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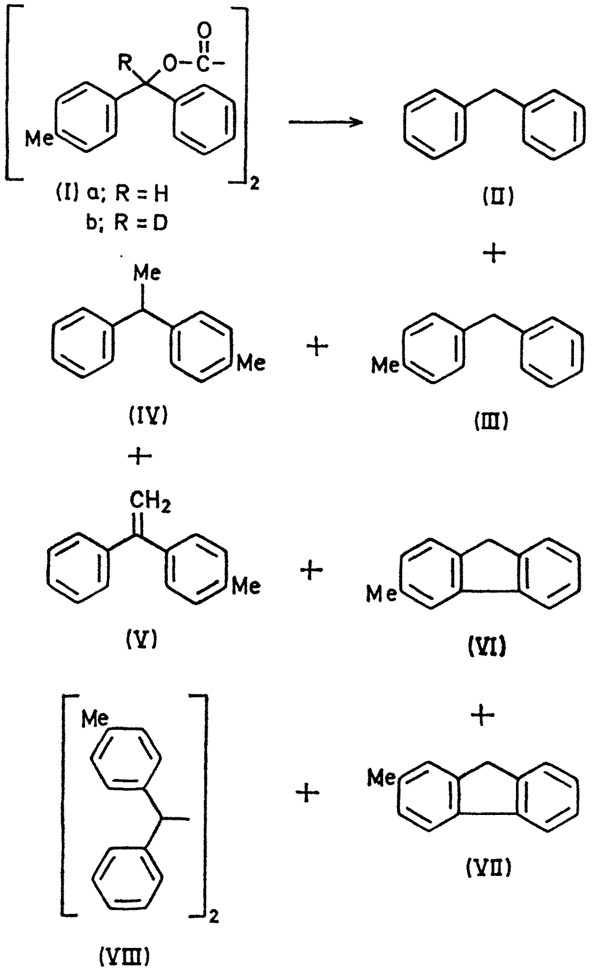
Summary The 2-methylfluorene recovered from the pyrolysis of bis [phenyl(*p*-tolyl)methyl] oxalate is shown to arise from fragmentation to a carbene, thereby providing the first example of a carbene-producing pathway competing with the production of radicals in oxalate pyrolysis.

PREVIOUS studies of the thermal decomposition of organic oxalates lacking a β-hydrogen have indicated that they fragment to produce radicals. Thus, the vapour-phase pyrolysis of diallyl[1] and dibenzyl[2] oxalates and the pyrolysis of benzhydryl oxalates[3] (neat and in diphenyl ether) gave products indicative of a radical process.

We now present results that establish a competing fragmentation to a carbene in the pyrolysis of bis-[phenyl-(*p*-tolyl)methyl] oxalate (Ia). Pyrolysis of the oxalate (Ia)† m.p. 83·5—85° gives seven products (II)—(VII) (see Scheme 1 and the Table).



SCHEME 1

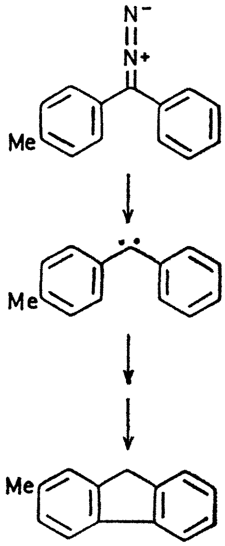
TABLE

T/°C	*Yield (mole/mole oxalate)*						
	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
650[a]	0·03	1·15	0·03	0·01	0·01	0·02	0·10
900[b]	0·007	0·20	0·03	0·002	0·02	0·06	0·40

[a] The sample, adsorbed on Chromosorb W, was introduced slowly into the hot tube at *ca.* 5 mmHg pressure.

[b] The sample was introduced dropwise as a benzene solution into the hot tube at *ca.* 95 mmHg pressure.

Although products (II)—(VI) can reasonably be imagined to result from radical processes, the formation of (VII) is more difficult to rationalise in these terms. The possibility that the carbene is a precursor of (VII) was suggested by the results of Jones and his co-workers.[4] They demonstrated the formation of 2-methylfluorene in the pyrolysis of phenyl(*p*-tolyl)diazomethane, a reaction that apparently proceeds by a multiple carbene rearrangement (see Scheme 2).[5]



SCHEME 2

We have tested the possibility of a carbene origin for the 2-methylfluorene obtained by oxalate pyrolysis. The deuteriated oxalate, (Ib) {96% [$^2H_1$] (mass spec.)}, was synthesised and pyrolysed in benzene at 950°. A necessary consequence of an α-elimination to the phenyl(*p*-tolyl)-carbene is a loss of the deuterium label. The 2-methylfluorene (VII) recovered from pyrolysis of the deuteriated oxalate had lost essentially all the deuterium label {99%

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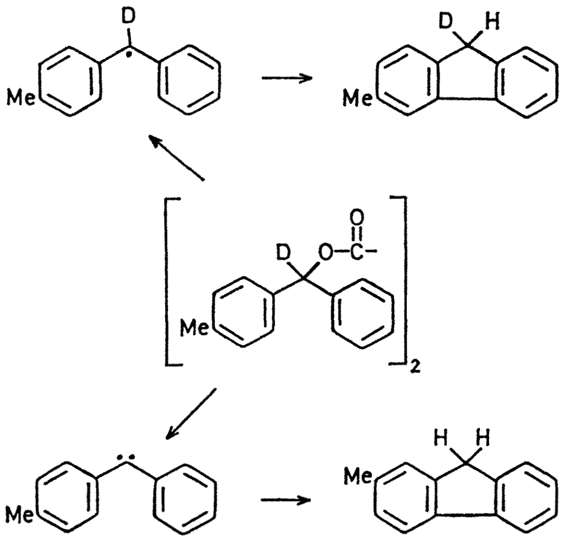
† All new compounds exhibited satisfactory spectral and analytical data.



SCHEME 3

$[^2H_0]$ (mass spec.)}. However, the 3-methylfluorene (VI) had retained, to a large extent, its label {12% $[^2H_0]$, 85% $[^2H_1]$, 3% $[^2H_2]$ (mass spec.)}. These results, combined with the work of Jones, strongly implicate two competing pathways for the production of methylfluorenes: a carbene route to 2-methylfluorene and a radical route to 3-methylfluorene (see Scheme 3).

The extent of carbene formation in this system is not very large, but it is mechanistically significant. Carbene intermediates should now be seriously considered as possible precursors to products that could be rationalised either by carbene or radical pathways. Several products in previously reported oxalate pyrolyses[1b] may arise, at least in part, by carbene routes, rather than the suggested radical pathways.

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