Pyrolytic Generation of Acyloxycarbenes and their Rearrangement to 1,2-Diketones

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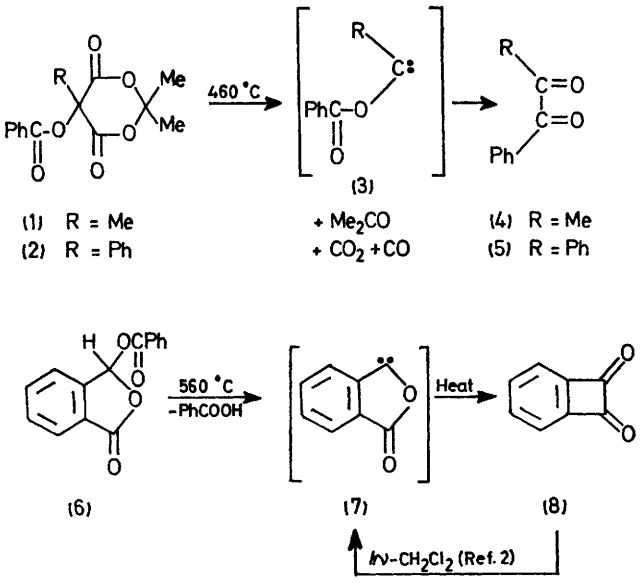
Summary Acyloxycarbenes are generated by thermal fragmentation of 5-benzoyloxy-1,3-dioxan-4,6-diones (**1** and **2**) and by thermal α-elimination of benzoic acid from 3-benzoyloxyphthalide (**6**).

IN an attempt to generate the elusive parent methyleneketen, $CH_2=C=C=O$, by a route akin to that used for higher members of the series[1] we examined the flash vacuum pyrolysis of the benzoate (**1**). Pyrolysis of (**1**) (460 °C, 0·5 mmHg) through silica gave a yellow liquid containing



acetone and 1-phenylpropane-1,2-dione (**4**; 90% yield). Similarly, pyrolysis of the phenyl-substituted benzoate (**2**) (460 °C, 0·05 mmHg) gave acetone and benzil (**5**; 81%). We propose that these diketones are formed by acyl migration in the intermediate acyloxycarbenes (**3**), which in turn arise from ketens $PhCO_2CR{=}CO$ by very ready decarbonylation.

Acyloxycarbenes are little known except for the cyclic species (**7**), generated photochemically in solution by irradiation of the strained diketone (**8**)[2,3] and studied by Staab and Ipaktschi.[2] We have now obtained this diketone (**8**; 33%) by pyrolysis of 3-benzoyloxyphthalide (**6**)[4] (560 °C, 0·1 mmHg). This process presumably involves α-elimination[5] of benzoic acid (91% crude yield) and ring contraction of the resulting carbene (**7**). The diketone (**8**) was accompanied by a small hydrocarbon fraction which contained biphenylene, probably formed by decarbonylation of (**8**).[6]

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