Rearrangement of Benzylidenecarbene formed by Pyrolysis of the Benzylidene Derivative of Meldrum's Acid at 560°

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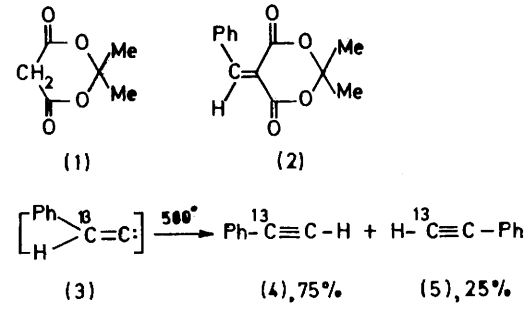
Summary Flash-vacuum pyrolysis of the benzylidene compound (**2**) gives acetone and phenylacetylene (98%); ^{13}C labelling shows that the presumed intermediate benzylidenecarbene (**3**) appears to undergo 75% of hydrogen migration and 25% of phenyl migration at 560°.

MELDRUM'S ACID[1] (**1**) readily undergoes condensation with carbonyl compounds[2] to give derivatives such as the benzylidene compound (**2**). The mass spectrum of (**2**) showed ready loss of acetone, carbon dioxide, and carbon monoxide from the molecular ion,[3] and this suggested[4] that pyrolysis of (**2**) might form benzylideneketen, PhCH:C-:C:O, or benzylidenecarbene, PhCH:C:.

Flash vacuum pyrolysis of (**2**) at 540°/0·1 mm through a silica tube packed with short lengths of silica tubing and with contact time *ca.* 0·1 s gave a liquid pyrolysate containing only acetone and phenylacetylene (98%, by g.c.). Labelled (**2**) was prepared from $Ph^{13}CHO$ containing 63% of ^{13}C, and similarly pyrolysed at 560°. The ^1H n.m.r. spectrum of the resulting labelled phenylacetylene in $CDCl_3$ showed a signal at δ 3·07 p.p.m. due to unlabelled PhC:CH flanked by strong sidebands with $J(^{13}C\text{–}C\text{–}H)$ 49·5 Hz and weak sidebands with $J(^{13}C\text{–}H)$ 251 Hz. Integration of the areas of these sidebands showed that the sample contained approximately 75% of (**4**), apparently formed by hydrogen migration in the presumed carbene intermediate (**3**), and 25% of (**5**) formed by phenyl migration. At present, however, we have no proof that migration occurs only at the carbene stage.



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