

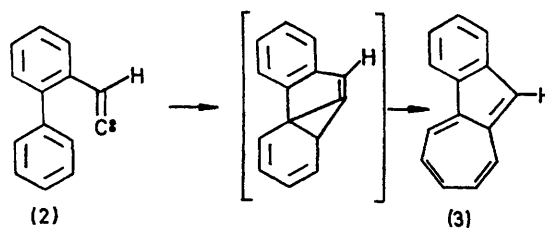
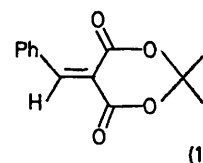
**Benzylidenecarbene as a Probable Intermediate in the Interconversion of
Ph¹³C≡CH and PhC≡¹³CH at 550 °C and 700 °C**

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Summary The rearrangement of labelled phenylacetylene is explained in terms of its equilibration with benzylidenecarbene at high temperatures.

In a previous communication¹ we reported that labelled benzylidenecarbene, Ph¹³CH=C:, generated by pyrolysis of labelled isopropylidene benzylidenemalonate (1) at 560 °C and 0.1 mmHg in a flow system, rearranged to form Ph¹³C≡CH and PhC≡¹³CH (75:25). We now find that this product ratio cannot be taken as a direct reflection of the migratory aptitudes of Ph and H because the migration is reversible.

Ph¹³C≡CH (63% ¹³C) was prepared from Ph¹³CHO by conversion to Ph¹³CH=CHBr followed by dehydrobromination with sodamide in liquid ammonia.² As expected from a previous labelling study of this elimination induced by butyl-lithium,³ the product, phenylacetylene, showed ¹H n.m.r. signals (CCl₄) centred at δ 3.07 due to PhC≡CH and



Ph¹³C≡CH [d, $J(^{13}\text{C}-\text{C}-\text{H})$ 49.3 Hz] only. Pyrolysis of the labelled phenylacetylene at 550 °C and 0.05 mmHg through a silica tube packed with short lengths of silica tubing and with contact time *ca.* 0.1 s gave colourless phenylacetylene which showed a new ¹H n.m.r. signal (d, J 250 Hz) due to PhC≡¹³CH (10% of labelled material). A similar experiment at 700 °C and 0.2 mmHg gave a pyrolysate containing Ph¹³C≡CH and PhC≡¹³CH in equal amounts as determined by integration of the ¹H n.m.r. signals.

The simplest interpretation of these results is that Ph¹³C≡CH undergoes ready migration of either H or Ph at high temperatures to give benzyliidenecarbene. Migration of Ph or H in benzyliidenecarbene then leads to PhC≡¹³CH and to the observed scrambling of the label at 700°. An earlier attempt⁴ to detect this rearrangement in Ph-¹³C≡CH or its anion, following the theoretical study of the

carbanion rearrangement by Van Dine and Hoffmann,⁵ was unsuccessful over the temperature range 65–178 °C.

The pyrolysis of biphenyl-2-ylacetylene provided supporting evidence for the generation of arylidenecarbenes from arylacetylenes. Pyrolysis at 550 °C and 0.03 mmHg gave a liquid pyrolysate containing the starting material, phenanthrene, and 1,2-benzazulene (**3**) in the ratio 94:3:3. Pyrolysis at 700 °C and 0.3 mmHg gave a blue crystalline pyrolysate containing phenanthrene and 1,2-benzazulene (72:28). We regard the formation of (**3**) as being strong evidence for the formation of the carbene (**2**) from the acetylene.

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⁵ G. W. Van Dine, and R. Hoffmann, *J. Amer. Chem. Soc.*, 1968, **90**, 3227.