Tetrahedron Letters, Vol.30, No.40, pp 5467-5468, 1989
Printed in Great Britain

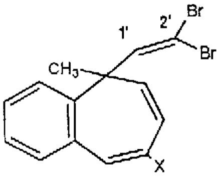
0040-4039/89 $3.00 + .00
Pergamon Press plc

A SOMERSAULTING REARRANGEMENT : FORMATION OF A REARRANGED ACETYLENE *VIA* A FOILED CARBENE

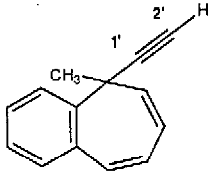
David W. Jones* and Robert J. Marmon
School of Chemistry, The University, Leeds, LS2 9JT, U.K.

Summary : Acetylene (3) is formed by the novel reaction of a foiled carbene (6).

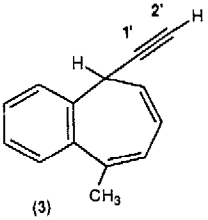
We have described the efficient (*ca.* 80% yield) conversion of (1; X = Br or H) into (2) and (3) (ratio 4.2:1) upon treatment with ^{n}BuLi.[1] Two mechanisms can be envisaged for the formation of the unexpected less abundant product (3). The product of initial halogen-metal exchange (4; X = H, Br or Li) could undergo an anion accelerated 1,5-vinyl shift (4; arrows) to give (5) which upon further reaction and work-up would give (3). The orientation of the migrating σ bond and the carbon orbital making the C-Li bond in (4) is appropriate for good overlap and accelerated 1,5-sigmatropy. This is in contrast to the orbital alignment in the lithium salt of (2) which is stable under the reaction conditions. Alternatively the carbene (6) or a related carbenoid could undergo the somersaulting rearrangement (6; arrows) to give (3).



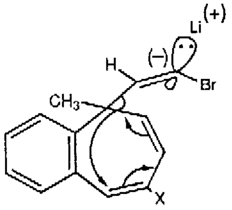
(1)



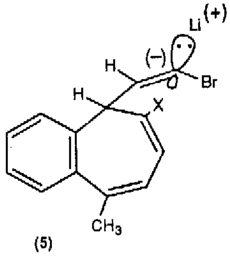
(2)



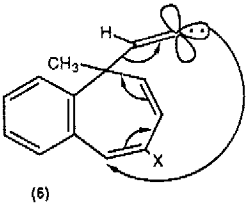
(3)



(4)



(5)



(6)

Since the first of these possibilities would be a novel type of anion acceleration of a pericyclic process,[2] whilst the second would be a novel reaction of a 'foiled carbene',[3] we sought to distinguish between them.

A simple way would be by ^{13}C-labelling at the 1'-position. Anion accelerated 1,5-sigmatropy would give (3) with the label still at C-1', conversely the somersaulting carbene rearrangement would give (3) labelled at C-2'.

^{13}C-Tagged (1) was prepared from benzyl chloride and potassium cyanide[4] that had been isotopically enriched by the addition of 5% ^{13}C-KCN. The synthesis was then carried out as previously described for unlabelled (1).[1,5] Reaction of ^{13}C-tagged (1) as detailed earlier[1] gave the labelled acetylenes (2) and (3).[6]

^{13}C N.m.r. was used to ascertain the site of the ^{13}C-tag in each acetylene; an integrated spectrum was produced for both compounds by doping the samples with chromium (III) acetylacetonate and using an inverse gated decoupling pulse sequence (fig. 1). Off resonance decoupling experiments unambiguously pinpointed the labelled carbons as C-2' for (3) and C-1' for (2).

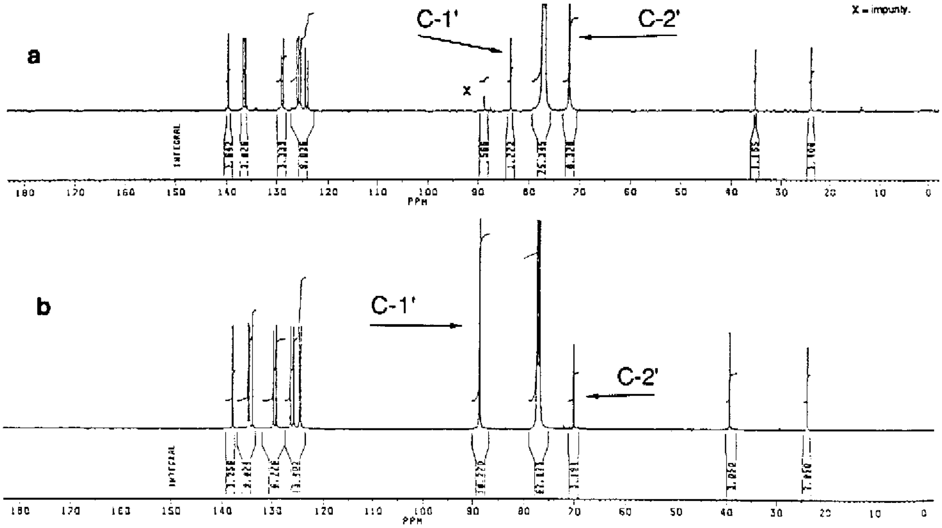


Fig. 1 Integrated ^{13}C spectra of acetylenes; **a** (3) and **b** (2).

Consequently acetylene (3) must have been formed by a somersaulting rearrangement of carbene (6) or its related carbenoid. There is to our knowledge no clear precedent for this rearrangement. Our search for a 1,5-shift of type (4; arrows) continues.

References

1. P.J. Battye and D.W. Jones, *J. Chem. Soc., Perkin Trans .1*, 1986, 1479.
2. For examples of a more usual type see : D.A. Evans and J.V. Nelson, *J Am. Chem. Soc.*, 1980, **102**, 774; L.A. Paquette, G.D. Crouse and A.K. Sharma, *ibid*, p.3972.
3. R.A. Moss and M. Jones, Jr. in 'Reactive Intermediates', Vol. 2, Wiley, New York, 1981, p.111.
4. M.B. Chkhaidze, Z.N. Morchiladze, Ts. I. Obolashvili and E.D. Oziashvili, *Analytical Chem. Symposia Series - Stable Isotopes*, H.-L. Schmidt, H. Förstel and K. Heinzinger (Eds.), 1982, **11**, p. 753.
5. G.N. Walker and D. Alkalay, *J. Org. Chem.*, 1971, **36**, 491.
6. Tagged products (2) and (3) were spectroscopically identical with the acetylenes described earlier.[1]

(Received in UK 17 August 1989)