Isomerisation of 1- and 2-Naphthylcarbene to Cyclobuta[*de*]naphthalene

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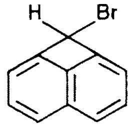
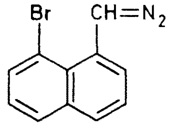
Summary Cyclobuta[*de*]naphthalene (**6**) is formed by flash vacuum pyrolysis of both 1- and 2-naphthyldiazomethane.

WHEREAS the intramolecular reactions of phenylcarbene have been thoroughly investigated[1] almost nothing is known of a related chemistry of 1-naphthylcarbene. Bailey and Shechter[2] reported the formation of 1-bromocyclobuta[*de*]naphthalene (**1**) by photolysis of 1-bromo-8-diazomethylnaphthalene (**2**). The reaction was considered to take place *via* bond formation between the carbene in position 1 and the bromine atom in position 8. The same reaction could not be achieved thermally, since (**2**) at 120 °C isomerised to 9-bromopyrazolo[4,3-*a*]naphthalene.



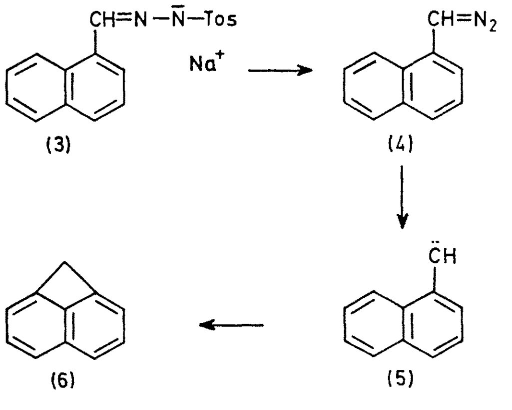
(1)



(2)

In continuation of our studies on $C_{11}H_8$ intermediates[3] we now report the direct thermal formation of cyclobuta[*de*]-naphthalene (**6**) from both 1- and 2-naphthylcarbene under flash vacuum pyrolysis conditions.

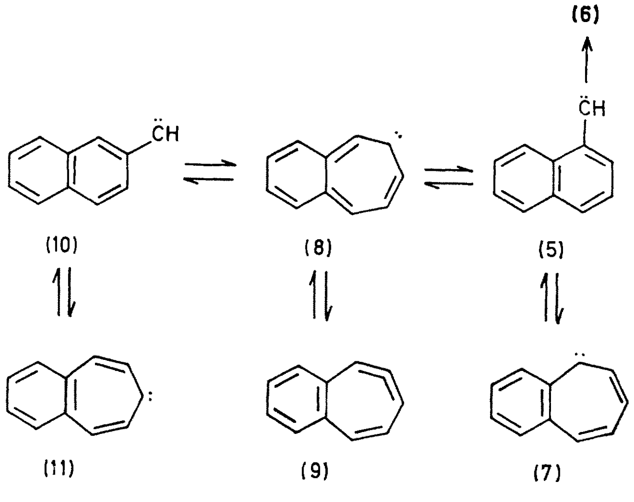
The dry sodium salt of 1-naphthaldehyde tosylhydrazone (**3**) was added slowly to a vertical quartz pyrolysis tube (30 × 2 cm), maintained at 10^{-3}—10^{-1} Torr and fitted with a loose plug of quartz wool *ca.* 10 cm below the top of the heated zone. The products were collected in a trap cooled in liquid N_2. Over the temperature range 400—800 °C, (**6**) was formed in up to 40% yield as shown spectroscopically, and was isolated by preparative g.l.c. ^1H n.m.r. spectrum: ($CDCl_3$; 100 MHz): δ 4·78 (s, 2H), 7·08 (d of d, J 5·6 and 1 Hz, 2H), and 7·3—7·6 (m, 4H). Since the n.m.r. coupling constants were slightly different from those reported by Shechter[2] for the compound obtained by reduction of (**1**), the ^{13}C n.m.r. spectrum of (**6**) was also recorded and found to agree in every respect with literature values.[2]



Tos = $MeC_6H_4SO_2$-*p*

Evidence that the formation of (**6**) takes place *via* the diazo compound (**4**) was obtained by first isolating (**4**) (ν 2150 cm^{-1}) from the decomposition of (**3**) at 130 °C *in vacuo*. A subsequent gas-phase pyrolysis at 600 °C (10^{-3}—10^{-4} Torr) was carried out by subliming (**4**) through a horizontal pyrolysis tube. Owing to the low volatility of (**4**), overall yields were low using this method, but n.m.r. spectroscopy and gas chromatography demonstrated that (**6**) was one of the major products.

Since there is ample precedent for carbene formation under the conditions used here,[1] the reaction if formulated as a simple isomerisation (formally a C–H insertion) of 1-naphthylcarbene (**5**). It is interesting to note that (**5**) presumably undergoes rapid ring expansion to benzocycloheptatrienylidene (**7**) (Scheme) under these conditions.[4] However, this latter reaction is unproductive at this temperature, and its reversibility allows the reaction (**5**) → (**6**) to dominate.



SCHEME

Even more astonishing was the observation that similar pyrolyses of 2-diazomethylnaphthalene likewise produced (**6**) in comparable yields. The formation of (**6**) is strong evidence for the carbene–carbene rearrangement (**10**) → (**8**) → (**5**) (Scheme). Previous work with methylnaphthylcarbenes had shown[5] that 3-Me-(**10**) would rearrange to 2-Me-(**11**), but not to 4-Me-(**8**). A further rearrangement of 2-Me-(**11**) led to trapping of the carbene by the methyl group, giving 2-vinylnaphthalene.[5] In our case, however, (**11**) bears no such 'trapping group,' and this route is, therefore, unproductive. Only the route *via* (**8**) [the stable form of which is (**9**)][6] to (**5**) leads to reaction. The irreversibility of the last step [(**5**) → (**6**)] displaces the whole equilibrium in this direction, even if the reaction

(**10**) → (**8**) is slower than (**10**) → (**11**). There is precedent for a reaction of the type (**10**) → (**5**) in the rearrangement of 2-quinolylcarbene to 1-naphthylnitrene, which commences already at 340 °C (10^{-3} Torr).[7]

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[3] C. Wentrup, E. Wentrup-Byrne, P. Muller, and J. Becker, *Tetrahedron Letters*, 1979, 4249; C. Wentrup and J. Benedikt, *J. Org. Chem.*, in the press.

[4] See ref. 1 (a), pp. 194—196.

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[6] R. L. Tyner, W. M. Jones, Y. Öhrn, and J. R. Sabin, *J. Amer. Chem. Soc.*, 1974, **96**, 3765.

[7] See ref. 1 (a), pp. 238—242; N. M. Lân, Ph.D. Dissertation, University of Lausanne (Switzerland), 1977.