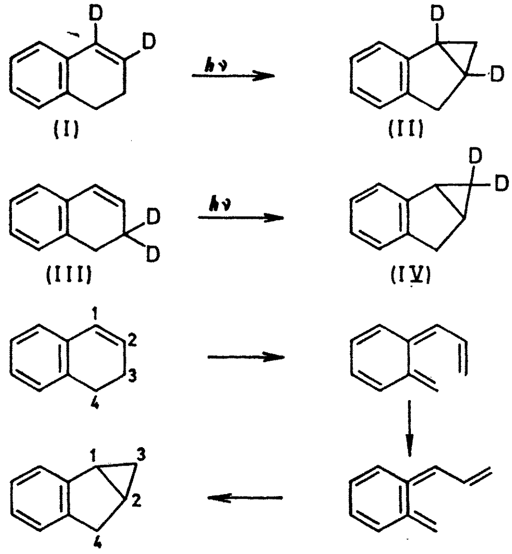
The Photoisomerisation of 1,2-Dihydronaphthalene

By R. C. COOKSON,* MISS S. M. DE B. COSTA, and J. HUDEC
(*Chemistry Department, The University, Southampton* SO9 5NH)

Summary Separate deuterium labelling of the olefinic and of a pair of methylene hydrogen atoms in 1,2-dihydronaphthalene shows that its photochemical rearrangement to benzobicyclo[3,1,0]hexene proceeds by opening and reclosure of the cyclohexadiene ring, rather than by hydrogen migration.

IRRADIATION with a medium-pressure mercury lamp through silica of dilute solutions of 1,2-dihydronaphthalene gave benzobicyclo[3,1,0]hexene, identical with an authentic sample,[1] as the main volatile product. A decision between migration of hydrogen and of carbon was reached by use of suitably deuteriated derivatives.



After irradiation of the 1,2-dideuterio-derivative (I) in ether (*c* 0·35%) with a 450 w. lamp for 3·5 hr., 36·5% of volatile product remained, consisting of the benzobicyclo[3,1,0]hexene (92%), tetralin (3·5%), 1,2-dihydronaphthalene (0·92%), 1,4-dihydronaphthalene (0·86%), and an unidentified product (2·2%).† The signals from the two tertiary protons in the tricyclic hydrocarbon (II) were completely absent from the 60 MHz. n.m.r. spectrum, which (CCl_4 solution with Me_4Si as external reference) in the non-aromatic region consisted of only two pairs of doublets, one at τ 9·02 and 10·0 (J 4·0) and the other at τ 6·8 and 7·2 (J −17·0).‡ The characteristic chemical shifts and coupling constants[2] identify the two methylene groups.

There is therefore no need to consider mechanisms involving migration of hydrogen atoms. Complete identification of the corresponding atoms in the reactant and product still required labelling of the two methylene groups. The 3,3-dideuterio-derivative (III) was therefore irradiated under the same conditions. The absence of signals from the two cyclopropane methylene protons in the product (IV) shows that in the isomerisation of 1,2-dihydronaphthalene the 3,4-bond is broken and new bonds are formed between C-3 and C-1 and between C-4 and C-2. The simplest mechanism that explains this consists of photochemical opening and shutting of the cyclohexadiene ring, as shown.

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† G.l.c. peak areas: the precise composition of the product depended on the solvent and concentration. Irradiation of the benzobicyclohexane under the same conditions gave mainly polymer, with 2% of 1,4-dihydronaphthalene.

‡ Protons at τ 6·8 and 9·02 are slightly coupled with each other.

[1] M. Pomerantz, *J. Amer. Chem. Soc.*, 1967, **89**, 694; J. Meinwald and P. H. Mazzocchi, *ibid.*, 1967, **89**, 696.
[2] R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron*, 1966, **suppl. 7**, 355; 1967, **23**, 1055.