

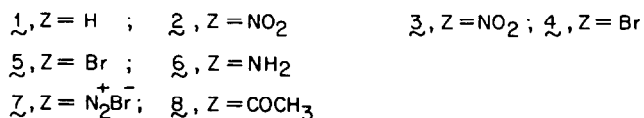
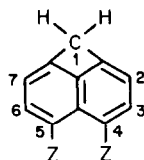
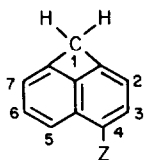
AROMATIC SUBSTITUTION AND ADDITION REACTIONS OF 1H-CYCLOBUTA[de]NAPHTHALENES

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Abstract: 1H-Cyclobuta[de]naphthalenes undergo electrophilic substitutions at their C-4 and their C-5 positions; photolytic bromination of 1H-cyclobuta[de]naphthalene yields 1,2,3,4-tetrabromo-1,2,3,4-tetrahydro-1H-cyclobuta[de]naphthalene.

1H-Cyclobuta[de]naphthalene (1) and many of its 1H-derivatives are now available.^{1a-j} The behavior previously elaborated for the above highly-strained peri-bridged system has emphasized reactions which occur at C-1 without rupture of the cyclobuta moiety.^{1g} Of concern therefore is that ring-opening of 1 occurs rapidly in acetic acid containing silver ion to yield 1-naphthylmethyl acetate.^{1g} Electrophilic aromatic substitutions of 1 and its derivatives which are synthetically useful might thus be limited because of rapid competitive ipso ring-rupture reactions of their cyclobuta units. The behavior of 1 with electrophilic reagents that effect aryl substitution is now reported. Photolytic halogenation resulting in addition to a benzenoid unit in 1 is also described.



Nitric acid in sulfuric acid-acetic acid converts 1 at ~25°C to 4-nitro-1H-cyclobuta[de]naphthalene (2, 85%) and 4,5-dinitro-1H-cyclobuta[de]naphthalene (3, 6%).^{1k} At 30°C 2 reacts with nitric acid in sulfuric acid to give 3 (89%). Nitration of 1 and 2 at other positions and ring-opening of the cyclobuta moieties in 1, 2 and 3 were not observed.

Bromine and ferric bromide effect conversion of 1 at 0°C to 4-bromo-1H-cyclobuta[de]naphthalene (5, 94%). Bromide 5 was also prepared by reduction of 2 with aluminum amalgam in ethyl ether-ethanol-water at 30°C to 4-amino-1H-cyclobuta[de]naphthalene (6, 80%), diazotization of 6 with nitrous and hydrobromic acids at 0°C and then heating 1H-cyclobuta[de]naphthyl-4-diazonium bromide (7) with cuprous bromide. Bromination of 5 with bromine and ferric bromide occurs smoothly to give 4,5-dibromo-1H-cyclobuta[de]naphthalene (4, 89%).

Friedel-Crafts acylations of 1 may also be effected without rupture of the cyclobuta moiety. Thus reaction of 1 with acetyl chloride in methylene chloride/aluminum chloride at

25°C yields 4-acetyl-1H-cyclobuta[de]naphthalene (8, >61%). Diacetylation of 1 with acetyl chloride/aluminum chloride in 1,2-dichloroethane failed.

Ring-opening thus does not occur in the reactions of 1 with nitric and sulfuric acids, bromine and ferric bromide, and acyl chlorides with aluminum chloride. Various electrophilic substitution reactions of 1 and its derivatives now appear to be feasible synthetically. Of further note is that electrophilic substitutions of 1H-cyclobuta[de]naphthalenes occur so selectively at C-4 and C-5. The impressive regiospecificities observed for substitution of 1 and its derivatives presumably have their origins in that bridging at the *peri* position with a single carbon atom moiety and maintenance of planar ring systems lead to severe compression in the front end and to significant bond lengthening and angle widening in the rear end of a naphthalene.^{11,m}

Photolysis of bromine and 1 in carbon tetrachloride yields the single adduct, 1,2,3,4-tetrabromo-1,2,3,4-tetrahydronaphthalene (9, mp 119-121°C). On the basis of its NMR, conformational effects in the presumed homolytic addition processes and by analogy with the products from naphthalene^{1n-q}, 9 is assigned as *trans-cis-trans*.^{1r} Of synthesis value is that 9 is dehydrobrominated by 1,5-diazabicyclo[5.4.0]undec-2-ene (DBU) to 2,4-dibromo-1H-cyclobuta[de]-naphthalene (10, 74%). Addition of halogen to 1 and then elimination of the tetrahalo adducts thus is an entrée to 2,4-disubstituted-1H-cyclobuta[de]naphthalenes. Of further interest is that 9 is converted to 1 (~100%) by sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al) in benzene.



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References and Notes

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