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POSSIBLE MECHANISMS FOR SOME REARRANGEMENTS INVOLVING SIGMA-COMPLEXES

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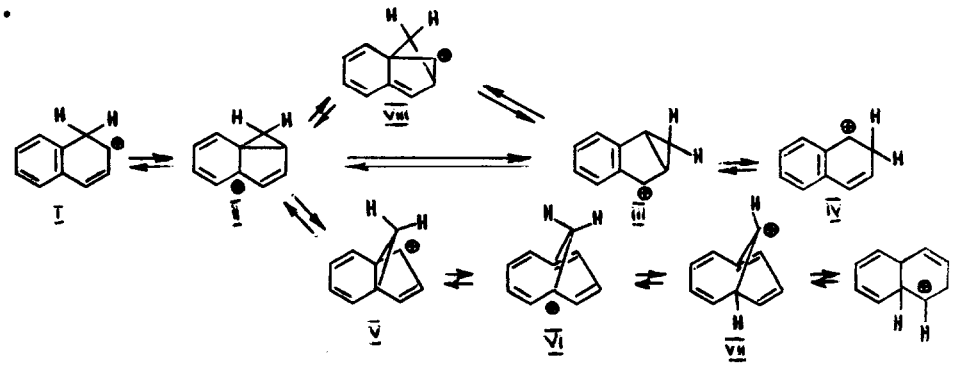
The scrambling of the ^{14}C isotopic label from position 1 into all positions of the naphthalene nucleus on treatment with water-promoted aluminium chloride (2,3) was interpreted as involving protonation of position 9, then either a series of Wagner-Meerwein 1,2-shifts, or a valence tautomerization to a cyclodecapentaene derivative. A third possible mechanism is suggested by recent publications, (4-6) namely the protonation of position 1 with the highest negative charge density, leading to the usual conjugate acid (sigma-complex) of naphthalene (I), (7) followed by circum-ambulatory migrations (8,9) of intermediately formed cyclopropane rings (II, III, V). Scrambling of the label from position 1 into 2 can be explained by the apparition of structures such as II-IV and into position 9 by structures like V - VII.

The migration of the cyclopropane ring around the sides of the other ring, might involve either a 1,3-migration as in the direct transformation II→III or two successive 1,2-shifts as in the sequence II⟶VIII⟶⟶III.



Rearrangements involving vinylcyclopropanes or cyclopropylcarbinyl derivatives are wide-known in cationic, (1o), anionic (11) or radicalic systems (12), and in photochemical processes (13). Some of these rearrangements have concerted mechanisms and involve six-membered transition states in which one or more double bond(s) are replaced by cyclopropane rings (14,15). Valency isomerizations of cyclopolyenes (16,17) like $(CH)_6$,(18), $(CH)_8$ and benzoderivatives (19), or $(CH)_{10}$, (2o), as well as of heterocycles,(21),also involve intramolecular formation and opening of cyclopropane rings in accordance with the Woodward-Hoffmann rules.

Although some reactions like the Jacobsen rearrangement (22), or the automerizations of ^{14}C-labelled toluene (23) and biphenyl (24) which proceed *via* sigma-complexes involve apparently 1,2-shifts of side-groups conserving the topology of the ring atoms, other reactions of sigma-complexes like those discussed above cause an appreciable reshuffling of the ring atoms in the sigma complex.

It was proved in the nitration of ^{14}C-labelled naphthalene that electrophilic aromatic substitutions with electron-acceptor substituents like NO_2 do not involve rearrangements of the ring atoms (2,3). Experiments are under way in our laboratory for investigating the electrophilic aromatic hydroxylation of naphthalene - 1 - ^{14}C, and the mechanism of the N.I.H. - shift. This shift of the *p*-standing hydrogen (25-29) or halogen (3o) atoms into the *m*-position on enzymatic (25-28,3o) or non-enzymatic (29) *p*-hydroxylation of substituted benzenes (acetanilide, (28,29) phenylalanine, (25, 26,3o) tryptophan (27)) was explained (28,29) as involving 1,2-shifts of side-atoms in the sigma-complex. It is possible that these atoms migrate together with the ring carbon atoms, and this is now being investigated in our laboratory.

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