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THE REACTIONS OF NITRENE FOR THE CONJUGATED π-SYSTEMS

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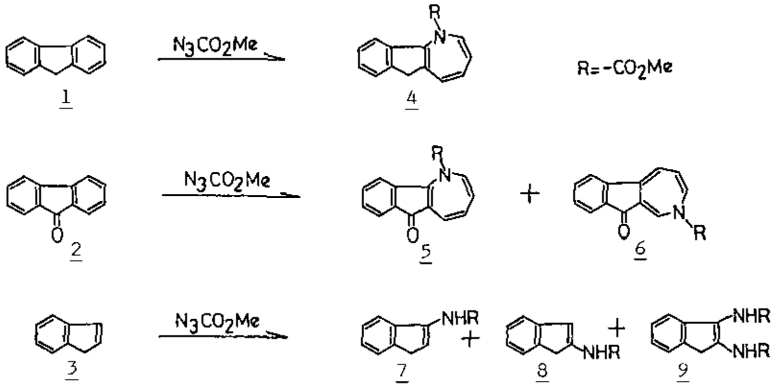
The addition reaction of methoxycarbonylnitrene, which was generated by a thermal decomposition reaction of methyl azidoformate, and conjugated π-systems was studied. When fluorene (1) and methyl azidoformate was heated at 130°C for 4h, regioselective addition to C_4-C_{4a} bond was occured to give indeno[3,2-c]azepine derivative (4) in 11.0 % yield. Under the similar conditions, 9-fluorenone (2) gave indeno[3,2-b]azepine derivative (5) and indeno[2,3-c]azepine derivative (6) in 3.8 % and 2.3 % yield, respectively. On the other hand, a thermal reaction of Indene (3) and methyl azidoformate did not give azepine derivatives but three aminoindene derivatives (7, 8, and 9).



These results may be explained by the Frontier Molecular Orbital (FMO) theory. The highest occupied molecular orbital (HOMO) of fluorene, 9-fluorenone, and Indene were shown in Fig. 1. The addition reaction of singlet nitrene to these conjugated π-systems took place at arrowed sites predominantly because of a efficient frontier orbital interaction between the HOMO of polyene and the LUMO of nitrene.

Some reactions and properties of indenoazepines were also discussed.

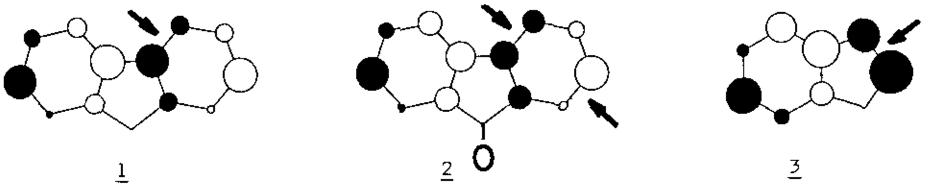


Fig. 1. The HOMO of compound 1, 2, and 3 calculated by CNDO/2 method.