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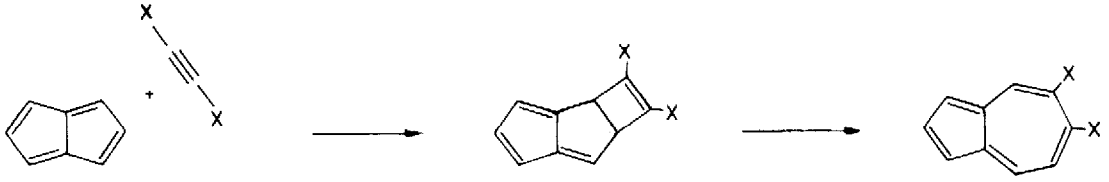
FRONTIER ORBITAL CONTROLLED CYCLOADDITION OF 2-AZAPENTALENES

Klaus Hafner+, Heinz-Gerd Kläs, and Michael C. Böhm
Institut für Organische Chemie der Technischen Hochschule, Petersenstr. 22,
D-6100 Darmstadt (Germany)

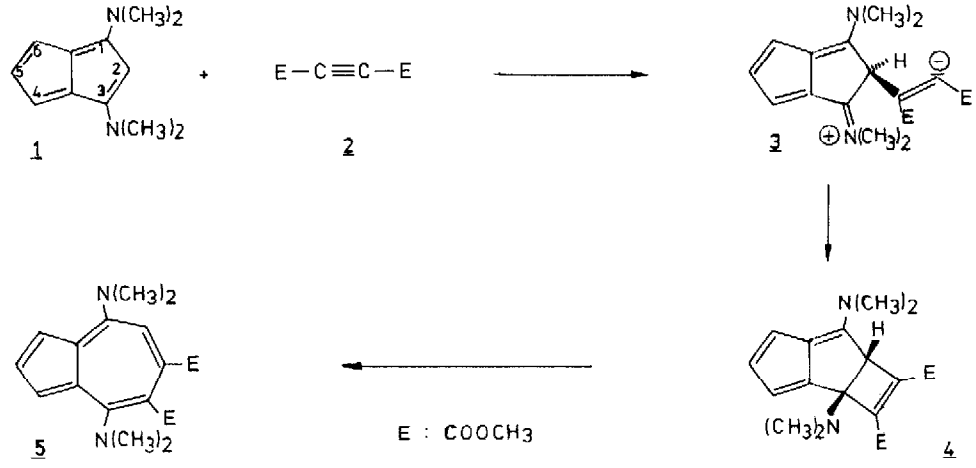
Summary: It is shown that cycloadditions of 1,3-bis(dimethylamino)pentalenes and their 2-aza-analogues with activated alkines are frontier orbital controlled whereas protonation is charge controlled.

Formal [2+2]-cycloadditions of pentalenes with activated alkines provide an interesting method



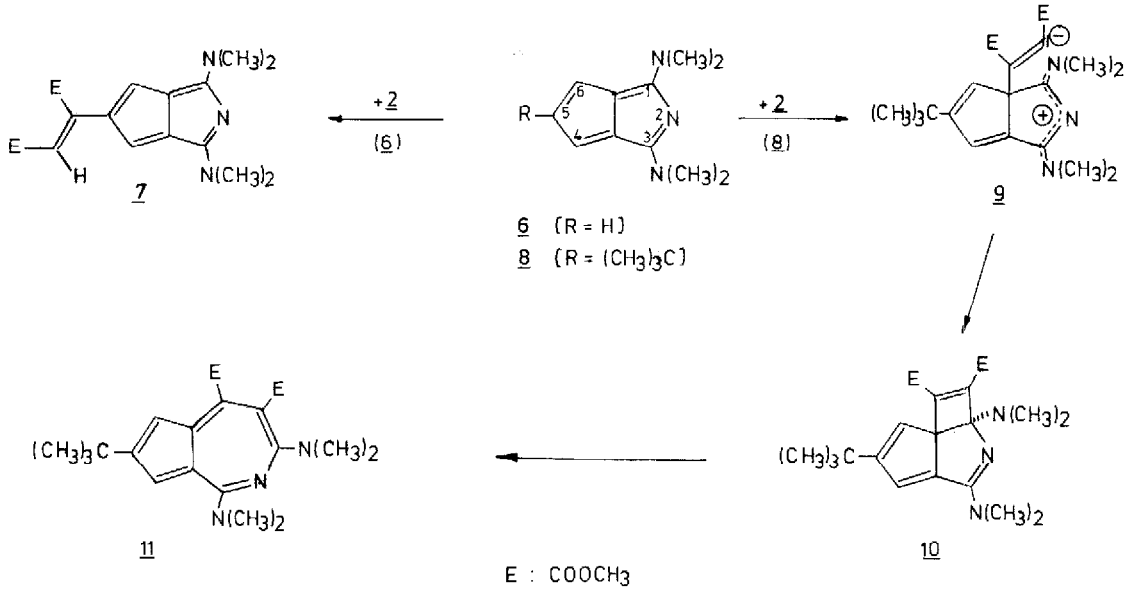
for the homologization of the 8π-electron system leading to azulenes[1].

1,3-Bis(dimethylamino)pentalene 1[2] reacts already at 0°C with dimethyl acetylenedicarboxylate 2 to give the azulene derivative 5[1b]. In analogy to cycloadditions of enamines with 2[3], the



1 2 3 4 5

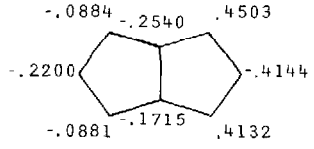
initially formed dipole 3 presumably undergoes cyclization to 4 which suffers valence isomerization to 5. Contrary to this finding, the aza-analogue of 1, 1,3-bis(dimethylamino)-2-azapentalene 6[4], reacts with 2 in a completely different fashion. Instead of a cycloadduct similar to 4 or its valence isomer 5, 72% of the substitutive addition product dimethyl 1,3-bis(dimethylamino)-2-azapentalen-5-yl-maleate 7[5] is formed at 0°C. Even if position 5 is substituted by a bulky group as in 8, products originating from the expected electrophilic attack of 2 at the ring nitrogen, the position of highest electron density, could not be detected. Due to the blocking of the 5-position, 5-tert.butyl-1,3-bis(dimethylamino)-2-azapentalene 8 combines with 2 at 0°C to furnish in 65% yield dimethyl 2-tert.butyl-6,8-bis(dimethylamino)-5-azaazulene-4,5-dicarboxylate 11 (yellow crystals, mp 164°C, UV (n-hexane): λ_{max}[nm] (log ε)= 207sh(4.17), 237sh(4.08), 252sh(4.13), 279(4.23), 340(4.44), 381sh(3.96), 456(4.06))[6]. The structure of 11



was deduced from its ^{1}H and ^{13}C nmr spectra[7] (^{1}H-NMR ($CDCl_3$): δ= 1.25(s,9H), 3.00(s,6H), 3.25 (s,6H), 3.82(s,3H), 3.95(s,3H), 6.45(s,1H, J=2Hz), 6.70(s,1H, J=2Hz); ^{13}C-NMR ($CDCl_3$) : δ= 31.9($(CH_3)_3C$), 39.3 and 40.6(2$(CH_3)_2N$), 51.6 and 52.4(2 OCH_3), 95.9(C-7), 114.8(C-3), 115.2 (C-3a), 118.2(C-1), 121.6(C-8a), 146.6(C-2), 156.5(C-4), 157.9(C-6)) and confirmed by an x-ray analysis[8]. Obviously 2 attacks 8 in the 3a- or 6a-position under formation of the dipolar intermediate 9 which reacts to the tricyclic system 10. A following valence isomerization leads to 11.

The different pathways of the reactions of 1, 6, and 8 with 2 can be explained by the dominance of the frontier orbital contribution[9] over the charge controlling term in the perturbation treatment of chemical reactivity[10]. Only if the Coulomb potential exceeds the frontier interaction the various net charges determine the course of the reaction. In case of frontier orbital control one has to analyse the localization of the highest donor orbitals in the pentalene series 1, 6, and 8.

The general characteristics of the calculated net charges (charge control) and the LCAO amplitudes of the HOMO (frontier control) are quite insensitive with respect to the calculation procedure involved. The results can be rationalized by HMO[11] or by semiempirical LCAO calculations (e.g. EHT[12]). In Fig. 1 the EHT net charges and in Fig. 2 the LCAO wave functions of the HOMO of the pentalenes are shown.



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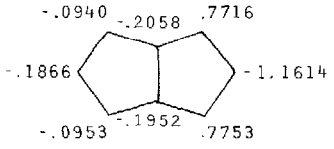

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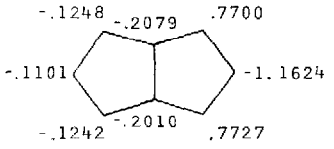

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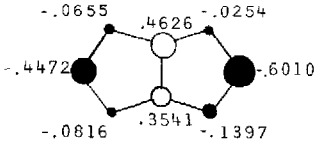
Figure 1: EHT net charges of 1, 6, and 8



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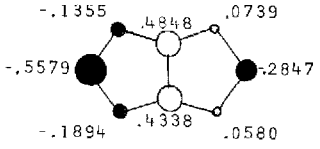

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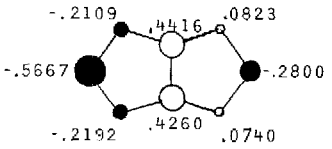

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Figure 2: LCAO coefficients of the HOMO of 1, 6, and 8

Inspection of both figures demonstrates that the reaction products of the additions are determined by frontier orbital control. If charge control would be the product determining factor, not only 1 should be attacked at position 2 but also 6 as well as 8 at the hetero atom. Fig. 2

shows that the adduct formations with 2 are influenced by frontier orbital interaction which leads in case of 1 to bond formation at C-2 followed by the closure of the four-membered ring at the electron-deficient centers C-1 or C-3. In the azapentalene 6 the HOMO is predominantly localized at C-5; thus frontier controlled attack is favoured at this position. In contrast to the reaction of 1 with 2 here the second step requires higher activation energy as the positions 4 and 6 carry higher net charges than 1 and 3 in the pentalene 1. Also in 8 the localization of the HOMO shows its maximum at C-5. The observed reaction product 11 is the result of a compromise between steric hinderance and maximum frontier orbital interaction, which is more efficient at C-3a and C-6a in comparison with N-2.

This shows that the experimental results of the reactions of 1, 6, and 8 with 2 can be explained by the dominance of frontier orbital interaction in comparison with charge control. On the other hand, charge control is active in the protonation of the pentalenes, e.g. electrophilic attack takes place at the electron-rich centers[2,4].

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